JOURNAL

OF

THE CHEMICAL SOCIETY.

ABSTRACTS OF PAPERS

ON

ORGANIC CHEMISTRY.

1897. Vol. LXXII. Part I.

LONDON:
GURNEY & JACKSON, 1, PATERNOSTER ROW.
1897.

Richard Clay and Sons, Limited,
london and bungay.

CONTENTS.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS:—

PART I.

Organic Chemistry

INSTRUCTIONS TO ABSTRACTORS,

GIVING THE

NOMENCLATURE AND SYSTEM OF NOTATION

ADOPTED IN THE ABSTRACTS.

1. Before beginning to write an abstract, it is desirable to read through the whole of the original paper, in order to form a judgment as to its importance, and as to the scale on which the abstract should accordingly be made.

2. The abstract should mainly consist of the expression, in the abstractor's own words, of the substance of the paper.

3. The abstract should be made as concise as possible, consistently with a clear and accurate statement of the author's results or theories, due regard being paid to their import.

4. If an abstract of a paper on the same subject, either by the author of the paper abstracted, or by some other author, has already appeared, note should as a rule be made of this fact. Important references to the researches of others quoted by an author should be reproduced in the abstract. Always employ figures instead of Roman numerals for references, thus :— *Annalen,* **221**, 92, instead of ccxxi, 92.

5. If an abstractor is acquainted with papers previously published by other authors containing statements either practically identical with, or opposed to, those in the paper abstracted, and to which no reference is made, he should notice their agreement or contradiction in a foot-note.

6. As a rule, details of methods of preparation or analysis, or, generally speaking, of work, may be omitted, unless such details are essential to the understanding of the results, or have some independent value.

Nomenclature.

7. Employ names such as *sodium chloride, potassium sulphate, ethyl acetate,* and use the terminals *ous* and *ic* only in distinguishing compounds of different orders derived from the same elementary radicle ; such, for instance, as mercurous and mercuric chloride, sulphurous and sulphuric acid.

8. Term compounds of metallic and alcoholic radicles with the group

OH, *hydroxides* and not hydrates ; for example, potassium hydroxide, phenyl hydroxide, the name hydrate being reserved for compounds supposed to contain water of combination or crystallisation. Compounds such as CH_3ONa, C_2H_5ONa, $C_7H_{15}ONa$, &c., should be termed sodium methoxide, ethoxide, heptyloxide, &c.

9. Apply the term *acid* only to compounds of hydrogen with negative radicles, such as HNO_3, H_2SO_4, H_3PO_4, and denote the oxides which form acids by names such as sulphuric anhydride, carbonic anhydride. Term salts containing an amount of metal equivalent to the displaceable hydrogen of the acid, *normal* and not neutral salts, and assign names such as hydrogen sodium sulphate, hydrogen disodium phosphate, &c., to the acid salts. Basic salts are as a rule best designated merely by their *formulæ*.

10. Use names such as *methane*, *ethane*, &c., for the normal paraffins or hydrocarbons of the C_nH_{2n+2} series of the form $CH_3{\cdot}[CH_2]_5{\cdot}CH_3$, &c. The isomeric hydrocarbons are usually most conveniently represented by names indicating their relation to methane ; for example, $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3$ = propylmethane ; $CH_3{\cdot}CH(CH_3)_2$ = isopropylmethane or trimethylmethane ; or, although less frequently, by names such as di-isopropyl.

11. Term the hydrocarbons C_2H_4 and C_2H_2 *ethylene* and *acetylene* respectively (not ethene and ethine). Distinguish the homologues of ethylene, whenever possible, by names indicating their relation to it, such as methylethylene, dimethylethylene, &c., denoting the di-derivatives of the form $C_nH_{2n+1}{\cdot}CH{:}CH{\cdot}C_nH_{2n+1}$ as α-, and those of the form $CH_2{:}C(C_nH_{2n+1})_2$ as β-compounds, thus : $CH_3{\cdot}CH{:}CH{\cdot}CH_3$ = α-dimethylethylene ; $CH_2{:}C(CH_3)_2$ = β-dimethylethylene. Similarly, use names such as methylacetylene and dimethylacetylene for the homologues of acetylene of the form $CH{\vdots}C{\cdot}C_nH_{2n+1}$ and $C_nH_{2n+1}{\cdot}C{\vdots}C{\cdot}C_nH_{2n+1}$. Adopt the name *allene* for the hydrocarbon $CH_2{:}C{:}CH_2$, and indicate the relation which its homologues bear to it in the same manner as pointed out for acetylene.

12. Distinguish all alcohols, that is, hydroxyl-derivatives of hydrocarbons, by names ending in *ol* ; such as quinol, catechol, resorcinol saligenol, glycerol, erythrol, mannitol, instead of hydroquinone, pyrocatechin, resorcin, saligenin, glycerin, erythrite, mannite. Compounds which are not alcohols, but which are at present distinguished by, names ending in *ol*, may be represented by names ending in *ole*, if a systematic name cannot be given. For example, write indole instead of indol ; furfuraldehyde instead of furfurol ; fucusaldehyde instead of fucusol. Ethers derived from phenols, such as $C_6H_5{\cdot}OCH_3$, &c., hitherto called anisol, anethol, &c., may be distinguished by names ending in *oil*, as anisoil and anethoil.

Alcohols should be spoken of as mono-, di-, tri-, or n-*hydric*, according to the number of OH groups.

13. Compounds analogous to the acids of the lactic series containing the group OH should be termed *hydroxy*-derivatives, and not oxy-derivatives ; for example, hydroxyacetic and not oxyacetic acid. Compounds containing the analogous groups C_2H_5O, C_6H_5O, $CH_3{\cdot}COO$, &c., should in like manner be termed ethoxy-, phenoxy-, acetoxy- derivatives. Thus

ethoxypropionic acid instead of ethyl-lactic acid; 3 : 4 diethoxybenzoic acid instead of diethylprotocatechuic acid; and acetoxypropionic acid instead of acetyl-lactic acid. Terms such as diethylprotocatechuic acid should be understood to mean a compound formed by the displacement of hydrogen-atoms in the hydrocarbon radicle of protocatechuic acid by ethyl, viz., $C_6H(C_2H_5)_2(OH)_2\cdot COOH$, and not $C_6H_3(OC_2H_5)_2\cdot COOH$, just as dibromoprotocatechuic acid is understood to be the name of a compound of the formula $C_6HBr_2(OH)_2\cdot COOH$.

14. The term *ether* should be restricted to the oxides of hydrocarbon radicles, and the so-called compound ethers should be represented by names similar to those given to the analogously constituted metallic salts (comp. 12).

15. Compounds of the radicle SO_3H should, whenever possible, be termed *sulphonic* acids, or failing this, *sulpho-compounds*: as benzenesulphonic acid, sulphobenzoic acid, and not sulfi-compounds. Compounds of the radicle $SO_2\cdot NH_2$ should be termed sulphonamides.

16. Basic substances should invariably be indicated by names ending in *ine*, as aniline, instead of anilin, the termination *in* being restricted to certain neutral compounds, viz., glycerides, glucosides, bitter principles, and proteids, such as palmitin, amygdalin, albumin. The compounds of basic substances with hydrogen chloride, bromide, or iodide should always receive names ending in *ide* and not *ate*, as morphine hydrochloride and not morphine hydrochlorate.

Notation.

17. Equations should *be omitted* unless essential to the understanding of the results; they, as a rule, should *not* be written on a separate line, but should "run on" with the text.

18. To economise space, it is desirable: 1, that *dots* should be used *instead of dashes* in connecting contiguous symbols or radicles, whenever this does not interfere with the clearness of the formula; 2, that formulæ should be shortened by the judicious employment of the symbols Me for CH_3, Et for C_2H_5, Pr^{α} for $CH_2\cdot CH_2\cdot CH_3$, Pr^{β} for $CH(CH_3)_2$, Ph for C_6H_5, Ac for $CO\cdot CH_3$, and Bz for $CO\cdot C_6H_5$; and 3, that formulæ should be written *in one line* whenever this can be done without obscuring their meaning. For example:

$CCl_3\cdot CH(OEt)_2$ instead of $CCl_3{-}CH{<}\begin{matrix}OC_2H_5\\OC_2H_5\end{matrix}$

$[CCl_3\cdot CH(OH)]_2S$ instead of $\begin{matrix}CCl_3{-}CHOH\\CCl_3{-}CHOH\end{matrix}{>}S$

$CH_2{:}CH_2$ instead of $CH_2{=}CH_2$

$CH{:}CH$ instead of $CH{\equiv}CH$

$CH{:}C\cdot CH_2\cdot CH_2\cdot C{:}CH$ instead of $\begin{matrix}CH_2{-}C{\equiv}CH\\|\\CH_2{-}C{\equiv}CH\end{matrix}$

$CHMe{:}CHPr^{\alpha}$ instead of $CH_3\cdot CH{=}CH\cdot CH_2\cdot CH_2\cdot CH_3$,

COOH·CH:CHMe·COOH instead of $\begin{array}{l}CH_3—C{=\!=}CH \\ \quad\;\; | \quad\;\; | \\ \;\;COOH\;\; COOH\end{array}$

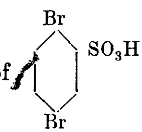
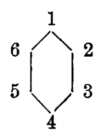
$CH_2Br·CBrMe_2$ instead of $\begin{array}{l}CH_3CH_3 \\ \quad \diagdown\!\diagup \\ \quad CBr \\ \quad\; | \\ \quad CH_2Br\end{array}$

$CEt_2Ac·COOEt$ instead of $\begin{array}{l}CH_3 \\ \;| \\ CO \\ \;| \\ C{<}\begin{array}{l}C_2H_5\\C_2H_5\end{array} \\ \;| \\ COOC_2H_5\end{array}$

$\begin{array}{l}CH_2·CHMe \\ \;| \\ CH_2·CHMe\end{array}{>}O$ instead of $\begin{array}{l}CH_2—CH·CH_3 \\ \;| \qquad\quad \diagdown \\ \;| \qquad\quad\;\; {>}O, \\ \;| \qquad\quad \diagup \\ CH_2—CH·CH_3\end{array}$

CHPh(OBz)·CH(OBz)·COOEt instead of
$C_6H_5·CH(O·CO·C_6H_5)·CH(O·CO·C_6H_5)·COOC_2H_5$.

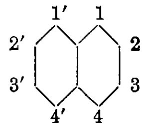
19. In representing the constitution of benzene derivatives, as a rule, merely indicate the relative positions of the radicles in the symbol of benzene by figures, instead of by means of the hexagon symbol, for example :—

Paradibromobenzenesulphonic acid, $C_6H_3Br_2·SO_3H$ [Br : SO_3H : Br = 1 : 2 : 4] instead of  the figures always being used in the order 

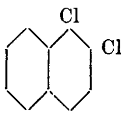
Relatively to the position 1, the positions 2 and 6 should always be spoken of as *ortho*-positions, 3 and 5 as *meta*-positions, and 4 as the *para*-position. It is better, however, in speaking of the derivatives of benzene, to express their constitution by giving them names such as 1 : 2 dibromobenzene, 1 : 3 dibromobenzene, &c., rather than by terming them ortho- or meta-dibromobenzene, &c.

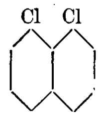
20. Moreover, in representing the constitution of derivatives of other "closed chain" hydrocarbons, do not, as a rule, employ graphic formulæ, but merely indicate the position of the radicles introduced in the following manner :—

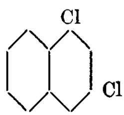
In the case of naphthalene, express the position of the radicles introduced in place of hydrogen relatively to the carbon-atoms common to the two "rings," and number the positions in the one ring 1, 2, 3, 4, and those in the other 1′, 2′, 3′, 4′ in the order shown by the annexed symbol :—

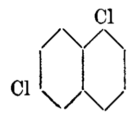


The dichloronaphthalenes, for example, are spoken of simply as 1 : 2 dichloronaphthalene, or dichloronaphthalene [Cl : Cl = 1 : 2], &c., thus :—

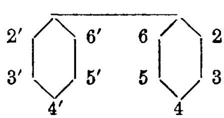
1 : 2 dichloro-naphthalene = 

1 : 1′ dichloro-naphthalene = 

1 : 3 dichloro-naphthalene = 

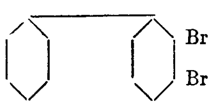
1 : 3′ dichloro-naphthalene = 

In the case of diphenyl, indicate the position of the radicles relatively to the carbon-atom of one C_6 group which is associated with the other C_6 group, and number the positions in the one group by the figures 2, 3, 4, 5, 6, and the corresponding positions in the other group by the figures 2′, 3′, 4′, 5′, 6′, as shown by the following symbol :

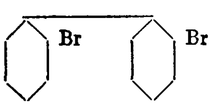


Thus the mono-derivatives, the bromodiphenyls, for example, are represented as

Bromodiphenyl [Br = 2]
" [Br = 3]
" [Br = 4]

and the two dibromodiphenyls 

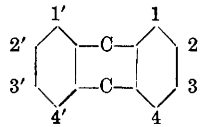
and



are respectively dibromodiphenyl [Br : Br = 2 : 3]

and dibromodiphenyl [Br : Br = 2 : 6′].

In the case of anthracene, employ the following symbol and indicate the position of the radicles relatively to the central C_2-group :



Examples :

Alizarin, $C_6H_4 \colon C_2O_2 \colon C_6H_2(OH)_2$ [OH : OH = 1 : 2].
Quinizarin, $C_6H_4 \colon C_2O_2 \colon C_6H_2(OH)_2$ [OH : OH = 1 : 4].
Anthraflavic acid, $C_6H_3(OH) \colon C_2O_2 \colon C_6H_3(OH)$ [OH : OH = 2 : 3′].

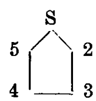
Purpurin, $C_6H_4 \colon C_2O_2 \colon C_6H(OH)_3$ [OH : OH : OH = 1 : 2 : 4].

In speaking of compounds such as these, their constitution may be represented by the names

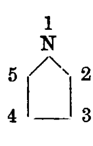
1 : 2 Dihydroxyanthraquinone	,,	= Alizarin.
1 : 4	,,	= Quinizarin.
2 : 3′	,,	= Anthraflavic acid.
1 : 2 : 4 Trihydroxyanthraquione		= Purpurin.

Always include the letters and figures indicating the constitution of derivatives of closed-chain hydrocarbons in square brackets.

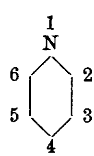
21. *In the case of thiophen*, express the position of the radicles introduced relatively to the sulphur atom by numbers, as shown by the following symbol :



In the cases of pyrroline and pyridine, indicate the position relatively to the nitrogen atoms as shown by the following symbols :

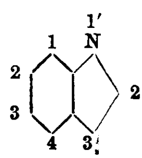


Pyrroline.

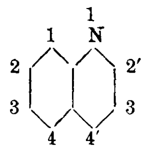


Pyridine.

In the case of indole, positions should be numbered as shown in the following symbol :—



In the case of quinoline, express the positions relatively to the carbon-atoms common to the two rings, and number the positions in the carbon ring 1, 2, 3, 4, and those in the nitrogen ring 1′, 2′, 3′, 4′, in the order shown by the annexed symbol :—



The Editor's decision, in all matters connected with the Abstracts, must be considered final.

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ON
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ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS :—

PART II.

General and Physical Chemistry.

Inorganic Chemistry.

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Analytical Chemistry.

JOURNAL

OF

THE CHEMICAL SOCIETY.

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

PART I.

Organic Chemistry.

Mixed Trimethylene Compounds. By LOUIS HENRY (*Compt. rend.*, 1896, **123**, 311—313).—The author has prepared some new trimethylene compounds by taking advantage of the different reaction aptitudes of the various halogens in mixed haloid derivatives (Abstr., 1883, 787).

Trimethylenic chloriodide, $CH_2Cl\cdot CH_2\cdot CH_2I$, is obtained by the action of trimethylenic chlorobromide on a molecular proportion of sodium iodide in presence of methylic alcohol. It is a colourless liquid which has a piquant odour, becomes brown when exposed to light, solidifies in solid carbonic anhydride and ether, forming crystals which melt at $-69\cdot5°$, and boils at 170—172° under ordinary pressure; sp. gr. $= 1\cdot904$ at 20°; vapour density $= 6\cdot98$ (calc. $= 7\cdot06$). The boiling point of this compound is exactly the mean of the boiling points of trimethylenic dichloride, 120°, and trimethylenic di-iodide, 224°.

Trimethylenic nitroxychloride, $CH_2Cl\cdot CH_2\cdot CH_2\cdot NO_2$, obtained by the action of the preceding compound on silver nitrate, is a colourless mobile liquid with a faint ethereal odour and piquant taste; sp. gr. $= 1\cdot267$ at 20°. It does not solidify in solid carbonic anhydride and ether, boils and decomposes slightly at 197° under ordinary pressure, and boils at 115—116° under a pressure of 40 mm.; vapour density, 4·13 (calc. 4·26). C. H. B.

Preparation of Cyanogen Bromide, Bromonitromethane and Dibromonitromethane. By ROLAND SCHOLL (*Ber.*, 1896, **29**, 2325). Compare Abstr., 1896, i, 585. Reply to Tscherniac (Abstr., 1896, i, 661 .

Preparation of Ammonium Ferricyanide. By N. TARUGI (*Gazzetta*, 1896, **26**, ii, 25—28).—Silver ferricyanide, precipitated from potassium ferricyanide solution, is well washed and treated with the corresponding quantity of ammonium chloride ; the filtrate, evaporated after filtering off the silver chloride, yields pure ammonium ferricyanide. If a standard solution of potassium ferricyanide is precipitated with standard silver nitrate, and standard ammonium chloride used to decompose the silver salt, an accurately standardised solution of ammonium ferricyanide can be obtained.

Bette (*Annalen*, 1837, **23**, 1) describes ammonium ferricyanide as crystallising in ruby red prisms which are stable in the air ; it is really obtained in tiny green crystals which become blue in the air, although its solutions are very stable if preserved in closed vessels.

W. J. P.

Ferricyanides, and their Use as Oxidising Agents. By GEORG KASSNER (*Arch. Pharm.*, 1896, **234**, 330—348).—Although a solution of potassium ferricyanide containing potassium hydroxide in addition is stable in the dark, it is partly decomposed when heated above 60°, or when exposed to direct sunlight ; under these circumstances ferric hydroxide is deposited, and the solution contains hydrocyanic acid and ammonia ; the decomposition is less when an alkali carbonate is present in place of the hydroxide, still less in the presence of an alkali hydrogen carbonate. An alkaline solution of the ferrocyanide hardly undergoes any such change when heated, and does not undergo it at all when it is exposed to light, except when air is not excluded. The author says that the view of these double cyanides as salts of ferri- and ferro-cyanic acids must be given up ; they are to be regarded as double salts in the old sense of the word, and in solution in excess of caustic alkali they are dissociated into the alkaline cyanide and colloidal ferric, or ferrous, hydroxide. When the ferricyanide acts as an oxidising agent, this ferric hydroxide is converted into ferrous hydroxide, which then forms ferrocyanide with the alkali cyanide present, the impetus to the whole series of reactions being found in the great tendency of alkali cyanides to form ferrocyanides with iron in any form. The spontaneous decomposition of the ferricyanide above 60° or in direct sunlight is explained by supposing that under these circumstances the colloidal ferric hydroxide is converted into the insoluble variety and precipitated ; some of the alkali cyanide present is then hydrolysed by the water.

In order, therefore, to obtain a permanent alkaline ferricyanide bath, for oxidising or bleaching purposes, the temperature should be kept below 60° and light should be excluded ; further, an excess of caustic alkali above the amount required by the equation should be avoided. To be regenerated, the bath should be treated with calcium plumbate (best already converted into calcium carbonate and lead dioxide), and carbonate anhydride passed in. Potassium carbonate is formed at the same time, but this can be removed by adding calcium plumbate, which is decomposed in the process into calcium carbonate and lead dioxide, the mixture required for the operation described above.

C. F. B.

Action of Morphine and of Acetanilide on Mixtures of Ferric Salts and Ferricyanides. By EDUARD SCHAER (*Arch. Pharm.*, 1896, **234**, 348—367).—Morphine reduces both ferric chloride and potassium ferricyanide, the former more strongly in neutral, the latter more strongly in acid solution. As a result of its action on a mixture of the two, a green coloration and, eventually, a blue precipitate are obtained. This precipitate consists mainly of Prussian blue, although it contains a little Turnbull's blue; on the whole, therefore, the ferricyanide has been reduced in preference to the ferric chloride.

Acetanilide also reduces both ferric chloride and potassium ferricyanide, but less strongly than morphine does. The precipitate that it produces in a cold neutral mixture of the two consists chiefly of Turnbull's blue; if the solution is hot, or if it is acid, however, Prussian blue is formed in larger amount.

Neither morphine nor acetanilide produces a blue precipitate in a mixture of potassium ferricyanide with soluble (dialysed) ferric hydroxide or ferric acetate. C. F. B.

Fulminates. By ARNOLD F. HOLLEMAN (*Rec. Trav. Chim.*, 1896, **15**, 159—160).—The solubility of purified mercury fulminate in water is at 12° 0·693—0·710, at 49° 1·7381—1·7835 gram per litre. The solubility of silver fulminate is at 13° 0·075, at 30° 0·180 gram per litre. One property common to both sodium fulminate and sodium cyanate is that of dissolving silver and thus forming double salts of the type NaCNO,AgCNO. J. J. S.

The Influence of the Presence of Acids on the Oxidation of Alcohols. By ANDRÉ BROCHET (*Bull. Soc. Chim.* [3], 1896, **15**, 16—20).—When treated with chlorine, isobutylic alcohol has been shown to give a chlorisobutaldehyde which, in presence of the hydrogen chloride formed during the reaction, condenses with the alcohol present in excess.

In order to eliminate the effect of the hydrogen chloride, the author treated a 10 per cent. aqueous solution of the alcohol with chlorine until no more of the gas was absorbed; the oil which separated on the surface of the water was found to contain isobutylic isobutyrate mixed with excess of the unaltered alcohol. After prolonged treatment with chlorine, the chlorinated derivatives of this salt appeared to be formed, particularly the α-chloro-compound, a liquid which boils at 183°, has sp. gr. = 0·998 at 15°/4°, refractive index $n_D = 1·435$ at 17°; on treatment with alkalis, this breaks up into isobutylic alcohol, and either α-chlorisobutyric acid, α-hydroxybutyric acid, or α-methylacrylic acid, according to the conditions of the reaction. The aqueous solution was found to contain a mixture of these acids with acetone and acetic and formic acids.

When the liquid was kept nearly neutral by the addition of sodium carbonate, isobutylic isobutyrate was formed as before, but the α-chloro-derivative and acetone only in very small quantity. Isobutylic alcohol in contact with a solution of sodium hypochlorite was found to yield 25 per cent. of the ethereal salt at the end of two months.

Lieben has obtained similar results with ethylic alcohol. Chlorine

reacts with a mixture of alcohol, water, and potassium carbonate, producing chloroform and ethylic acetate. When there is little or no water present, ethylic acetate is almost the sole product of the reaction. Bromine gives the same result. From these results it would appear that chlorine or bromine, acting on an alcohol in neutral or very slightly acid solution, behaves as an oxidising agent, and does not tend to displace hydrogen atoms in the molecule.

The conditions necessary for the production of aldehydes from alcohol by the aid of acid oxidising agents are also discussed.

M. W. T.

Action of Chlorine on Hot Isobutylic Alcohol. By André Brochet (*Bull. Soc. Chim.*, 1896, [3], **15**, 20—22).—The reaction is extremely complicated, but, as long as there is excess of the alcohol present, the chief product appears to be the compound $CMe_2Cl\cdot CH(OC_4H_9)_2$. On further chlorination, however, this breaks up into α-chlorisobutaldehyde and α-chlorisobutylic isobutyrate. Isobutyric acid, hydroxyisobutyric acid, chlorisobutyric acid, and α-methylacrylic acid are also products of the reaction.

If the action of the chlorine is prolonged, dichlorisobutaldehyde, boiling at 123°, is obtained together with isobutylic dichlorisobutyrate, which boils at 229° and has a sp. gr. = 1·155 at 15°/4°. Hexachlorethane appears to be one of the final products of the reaction. M. W. T.

Crystallised d-Mannose. By W. Alberda van Ekenstein (*Rec. Trav. Chim.*, 1896, **15**, 221—224. Compare Abstr., 1896, i, 272). —The author has studied the chief physical properties of crystallised *d*-mannose prepared by the decomposition of its phenylhydrazone by benzaldehyde (compare Abstr., 1895, i, 260). The pure syrupy *d*-mannose thus obtained was dissolved in various solvents, and the small crystals which separated after several weeks from a mixture of methylic alcohol and ether (1 : 1) were used for the purpose of inducing crystallisation in the other solutions. The substance thus obtained, after recrystallisation from 90 per cent. ethylic alcohol, melted at 132° without darkening, and was anhydrous, having the formula $C_6H_{12}O_6$. 100 parts of water at 17° dissolves 248 parts of *d*-mannose; 100 c.c. of absolute ethylic alcohol at 17·5° dissolves 0·4 gram. It has a somewhat bitter taste, and exhibits the property of multirotation. A 2 per cent. solution gave the following rotations:—After 3 minutes $[\alpha]_D = -13°·6$, after 6 hours (when constant) $[\alpha]_D = +14°·25$. The crystals are rhombic; $a:b:c = 0·319:1:0·826$.

The α-methylmannoside of E. Fischer was also examined; its solubility at 17° is, in water, 24·6 grams; in absolute alcohol, 1·5 gram; in 90 per cent. alcohol, 3·2 grams; in 80 per cent. alcohol, 7·8 grams per 100 c.c. of solvent. Its rotatory power in 1 per cent. aqueous solution is $[\alpha]_D = +82·5°$; in 8 per cent. solution, $+79·2°$; in 1 per cent. alcoholic solution, $+87·3°$. Its crystals are rhombic; $a:b:c = 0·9336:1:0·9249$.

The author has failed in his endeavours to prepare β-methylmannoside. A. C. C.

Decomposition of Monosaccharides by Alkalis. By FRIEDRICH FRAMM (*Pflüger's Archiv*, 1896, **64**, 575—599).—Moore's test is one of the best known of the monosaccharide reactions. Light has no influence on the decomposition. Equal molecular quantities of sodium or potassium hydroxide act in the same way on *d*-glucose. In the product, a considerable quantity of sugar is left, which may be estimated by Allihn's method; various products of oxidation (formic, acetic, oxalic, and especially lactic acids—Beilstein, Tollens), and certain brown products (glucic, saccharumic, japonic, and melassic acids) have been described.

The exclusion of air lessens the decomposition, and it is the products of oxidation with which this paper is specially concerned. In the case of *d*-glucose, only aldehyde and formic acid were identified among the products of oxidation. Galactose yields the same two substances. *d*-Fructose yields formic acid, and a doubtful trace of aldehyde. When air is excluded, *d*-fructose is more readily decomposed than *d*-glucose and galactose. Arabinose yields the same oxidation products as the hexoses.

W. D. H.

Aldazines, Ketazines, and Benzosazones of Aldoses and Ketoses. By ERNST DAVIDIS (*Ber.*, 1896, **29**, 2308—2311. Compare Abstr., 1895, i, 33, and 216).—*Glucosealdazine*, $C_6H_{12}O_5{:}N{\cdot}N{:}C_6H_{12}O_5$, is obtained by heating finely-powdered glucose with hydrazine hydrate (2 mols.) and methylic alcohol, on the water bath; this being a general method for the production of aldazines and ketazines of sugars; it is a white, microcrystalline powder, and sinters about 80°, when it begins to decompose, melting indefinitely at 100°. It is very hygroscopic, dissolves readily in methylic alcohol and in water, the solution being neutral; it is insoluble in ether, chloroform, and benzene. The substance does not decompose in cold, aqueous solution, and is also indifferent towards dilute, aqueous alkalis; hydrolysis with dilute acids resolves it into glucose and hydrazine.

Arabinosealdazine, $C_5H_9O_4{:}N{\cdot}N{:}C_5H_9O_4$, closely resembles glucosealdazine, and is obtained from arabinose in a similar manner.

Fructoseketazine, $C_6H_{12}O_5{:}N{\cdot}N{:}C_6H_{12}O_5$, is a micro-crystalline, yellowish powder, which is less hygroscopic than the foregoing substances.

Glucosebenzosazone, $OH{\cdot}CH_2{\cdot}CH(OH){\cdot}[C({:}N{\cdot}NHBz)]_3{\cdot}CH{:}N{\cdot}NHBz$, is obtained when glucose is heated with benzhydrazide and very dilute caustic soda for $1\frac{1}{2}$ hour on the water bath; it crystallises in yellowish-brown leaflets, and melts at 256—257°. Levulose gives rise to the same substance.

The author has observed that arabinosebenzhydrazide melts at 211—212° instead of 184°, and dextrosebenzhydrazide at 195—196° instead of 171—172° (compare Wolff, Abstr., 1895, i, 216).

M. O. F.

Composition of Wood Gum. By SAMUEL W. JOHNSON (*J. Amer. Chem. Soc.*, 1896, **18**, 214—222).—Wood gum is abundantly extracted from the wood of deciduous trees by cold, weak (2—10 per cent.) solutions of sodium hydroxide, and is thrown down again on neutralisation

or on the addition of alcohol. On hydrolysis, it yields xylose. Wheeler and Tollens (*Annalen*, **254**, 320), &c., gave the formula $C_6H_{10}O_5$ for wood gum. The author shows by means of numerous analyses that wood gum obtained from ground maize cob is really the anhydride of xylose, that is, it is xylan, and has the composition $C_5H_8O_4$. The analysis is an extremely difficult operation as the compound has such a great avidity for water; the hygroscopic moisture is best determined by heating the substance to 110—112° in a vacuum.

The wood gum obtained from the American white or grey birch (*Betula alba*) has the composition $C_4H_6O_3$, and does not yield xylose on hydrolysis. This compound and its products of hydrolysis are being further investigated.

Dilute alkali extracts from vegetable ivory a substance similar to wood gum, which when hydrolysed yields mannose (compare Reiss, *Ber.*, 1889, **22**, 609), and, according to the author, has the composition $C_6H_{10}O_5$. He terms it mannan, and it is beyond doubt identical with Reiss's seminin and Tollens's paramannan. J. J. S.

Action of Alkalis on Neutral Aliphatic Nitramines. By ANTOINE P. N. FRANCHIMONT and H. VAN ERP (*Rec. Trav. Chim.*, 1896, **15**, 165—173. Compare Van Erp, Abstr., 1895, i, 590). When nitrohydantoïn is treated with baryta water, it yields nitrous acid and other products, but not nitraminoacetic acid as the authors expected. Nitromethylhydantoïn, $\begin{array}{l}CH_2\cdot N(NO_2)\\ \vert \\ CO\cdot NMe\end{array}\!\!>CO$, and nitrolactylcarbamide, $\begin{array}{l}CHMe\cdot N(NO_2)\\ \vert \\ CO\cdot NH\end{array}\!\!>CO$, also yields nitrous acid under similar treatment, whereas nitroacetonylcarbamide, $\begin{array}{l}CMe_2\cdot N(NO_2)\\ \vert \\ CO\cdot NH\end{array}\!\!>CO$, gives no trace of nitrous acid even after boiling with baryta water. It thus appears that in order to yield nitrous acid, the nitramine must have an atom of hydrogen attached to the carbon atom to which the nitramine group is directly united.

The authors have prepared *butylmethylenimine*, $C_4H_9N{:}CH$, by Henry's method (*Bull. Acad. R. Belg.*, 26—29, 1893—1895). Normal butylamine dissolved in an equal volume of water was added to a cold 40 per cent. solution of methanal; an oily liquid of sp. gr. 0·886 at 15° was thus obtained, which is probably *butylaminomethylic alcohol*, $C_4H_9\cdot NH\cdot CH_2\cdot OH$. It cannot be distilled without undergoing decomposition, and when treated with cold aqueous potash, it yields butylmethylenimine; this distils at 146—149° (10—12 mm.), and has a sp. gr. = 0·8772 at 15°. It combines in the cold with sulphuric acid, and the solution thus obtained when diluted yields methanal; nitrosyl sulphate, however, has no action on the compound. The imine yields a white precipitate with mercuric chloride and a silver mirror with silver nitrate, it precipitates the hydroxides from ferric chloride and copper sulphate solutions, and it combines with oxalic and picric acids. When reduced with sodium and alcohol, it yields primary butylamine, and methylbutylamine (?), and when heated with potash and water

at 150° for 6 hours, it yields formic acid and butylamine. These facts support Erp's views (Abstr., 1895, i, 590) regarding the action of alkalis on nitramines. Thus, on heating with potassium hydroxide, the nitramine is first decomposed into nitrous acid and an imine, but the latter undergoes further decomposition into a primary amine and formaldehyde; this, however, by the action of the alkali, is converted into formic acid. J. J. S.

Methylallylnitramine, an Isomeride, and their Bromine Derivatives. By HERM. UMBGROVE and ANTOINE P. N. FRANCHIMONT (*Rec. Trav. Chim.*, 1896, **15**, 195—210).—The chief object of this research was to ascertain whether a mixed nitramine of the general formula $RR'N\cdot NO_2$ containing one unsaturated radicle would resemble in its general properties a nitramine containing an aromatic radicle on the one hand, or one containing two alkyls on the other, the former bearing a much closer resemblance than the latter to the nitramides, on account of the more negative character of the aromatic radicle. Caustic alkalis, for instance, cause the separation of the benzyl group from the nitrogen in methylbenzylnitramine, whilst in methylethyl- and methylbutyl-nitramine the alkyl groups are not affected.

Methylallylnitramine, $CH_2{:}CH\cdot CH_2\cdot NMe\cdot NO_2$, was prepared both by the action of the potassium derivative of methylnitramine on allylic iodide and also by heating a mixture of potassium hydroxide, methylnitramine and allylic bromide, methylic alcohol being employed as a solvent in both methods. It is a colourless, refractive liquid, boils at 95—96° (18 mm.), decomposes when distilled under atmospheric pressure, has sp. gr. 1·1015 at 15°, and is almost insoluble in water, but soluble in all the ordinary organic solvents. When it is heated with an aqueous solution of potassium hydroxide in a sealed tube, nitrous acid, methylamine and an aldehyde, probably acraldehyde, are formed. It therefore behaves like benzylmethylnitramine, and not like a nitramine containing only alkyl groups.

The authors consider it very probable that methylallylenimine, $CH_2{:}CH\cdot CH{:}NMe$, is first formed together with nitrous acid in this reaction, and that this then gives rise under the influence of alkali and water to acraldehyde and methylamine. The above imine could not, however, be isolated (compare preceding abstract).

On oxidation with silver oxide, methylallylnitramine yielded nitrous acid, methylamine and probably acrylic acid; with weak aqueous potassium permanganate, it was hoped that a *methyldihydroxypropylnitramine* would be obtained; this was not isolated, but its *dibenzoate*, $OBz\cdot CH_2\cdot CH(OBz)\cdot CH_2\cdot NMe\cdot NO_2$, crystallised from ether in colourless needles, melting at 102°.

Methylallylnitramine combines with bromine in chloroform solution forming *methyl-2:3-dibromopropylnitramine*, a liquid of sp. gr. = 1·945 at 15°, which on cooling crystallised in large, monoclinic crystals, melting at 23°. It is insoluble in water, but dissolves in all the ordinary organic solvents. Attempts to convert this by hydrolysis into the dihydroxy-compound failed, although a small quantity of its dibenzoate, above described, was obtained.

From the lower fractions obtained during the fractional distillation of the products of the action of allylic bromide on the potassium derivative of methylnitramine, an isomeride of methylallylnitramine was obtained boiling at 51—52° (18—20 mm.). It is a colourless, mobile liquid, having a powerful odour, and of sp. gr. = 1·047 at 15°. It is distinguished from methylallylnitramine by its lower boiling point, lower specific gravity and by its different behaviour with caustic alkalis and sulphuric acid. When heated in a sealed tube with a solution of potassium hydroxide, it yields allylic alcohol and a gas, which probably is nitrogen. In the reaction of allylic bromide or iodide with the silver derivative of methylnitramine, both these isomeric nitramines were obtained in about equal proportions. This isomeride combines with 2 atoms of bromine in chloroform solution, yielding a substance which crystallises in colourless needles, melting at 65°, isomeric with the dibromo-derivative above described (compare following abstract). A. C. C.

Methylnitramine, Dimethylnitramine, and one of its Isomerides. By ANTOINE P. N. FRANCHIMONT aud HERM. UMBGROVE (*Rec. Trav. Chim.*, 1896, **15**, 211—220).—The observation that methylnitramine which has been somewhat strongly heated loses to some extent its power of crystallising readily, induced the authors to study the action of heat on that substance. When submitted to distillation, the temperature rises from below 100° to 187°, the products obtained being nitrous oxide, methylic alcohol, water, an isomeride of dimethylnitramine and dimethylnitramine (b. p. 187°) itself. The isomeride is distinguished from dimethylnitramine by its boiling point (112°), by its behaviour with strong sulphuric acid, with which it reacts vigorously, and by producing an immediate coloration in an acetic acid solution of α-naphthylamine. The quantitative relations between the above products were so dependent on the conditions under which the heating was effected, that it is impossible to represent the change by means of an equation; moreover, small quantities of nitrogen and of an oil (? a pyridine base) were also formed. The mechanism of this change is discussed, but the authors are unable at present to suggest any satisfactory explanation. By the action of methylic iodide on the silver derivative of methylnitramine, two dimethylnitramines are formed, one being the ordinary compound (b. p. 187°), whilst the other is apparently identical with the isomeride above mentioned (b. p. 112°). Its sp. gr. = 1·079 at 20°. The isomeric nitramine, when heated with an aqueous solution of potassium hydroxide in a sealed tube, yields methylic alcohol and nitrogen. (Compare preceding abstract for an analogous decomposition of the isomeride of allylmethylnitramine.) The authors suggest provisionally that the formula of the isomeric methylnitramine is NMe⋮NO·OMe. A. C. C.

Action of Alkylic Iodides on Hydroxylamine. By CORNELIS A. LOBRY DE BRUYN (*Rec. Trav. Chim.*, 1896, **15**, 185—186. Compare Abstr., 1894, i, 569).—The author confirms Dunstan's statement (Dunstan and Goulding, Proc., 1896, 72) that the product obtained by

the action of methylic iodide on hydroxylamine consists of trimethylhydroxylamine hydriodide and two hydriodides of hydroxylamine.

J. J. S.

Nitracetonitrile. By ROLAND SCHOLL (*Ber.*, 1896, **29**, 2415—2421).—Attempts to synthesize nitracetonitrile by the action of cyanogen bromide on sodium nitromethane having resulted in the production of bromonitromethane, the behaviour of iodacetonitrile towards silver nitrite has been studied.

Iodacetonitrile is conveniently prepared by heating chloracetonitrile (112 grams) with finely-powdered potassium iodide (300 grams) and methylic alcohol (300 grams) for 3 hours on the water bath. It is a heavy, colourless oil, which boils, and in part decomposes, at 182—184° under a pressure of 720 mm. When it is treated with silver nitrite, action occurs spontaneously, being accompanied by very rapid rise of temperature; if the mixture is cooled, it proceeds slowly, and a yellow double salt of silver iodide with an organic substance is produced, yielding a volatile oil when treated with boiling water.

Cyanomethazonic acid, $C_4H_2N_4O_3$, is obtained by adding, in small quantities at a time, a mixture of silver nitrite and sand to a hot solution of iodacetonitrile in benzene; it is a viscous, yellowish oil, and boils at 160—162° (uncorr.) under a pressure of 12 mm. The substance explodes when rapidly heated under atmospheric pressure, and the action of concentrated hydrochloric acid in sealed tubes at 60° gives rise to considerable quantities of ammonium chloride and oxalic acid, along with a small proportion of hydroxylamine; concentrated sulphuric acid liberates nitrous oxide, and, on warming the liquid, carbonic anhydride and carbonic oxide are produced, probably arising from oxalic acid. Fuming nitric acid dissolves the substance, and is without action on it when boiled. Cyanomethazonic acid dissolves readily in alkalis, but is not precipitated when the solution is rendered acid; thus dilute sulphuric acid causes the liquid to effervesce, and liberates hydrogen cyanide, ether extracting an oil which deposits crystals melting at 105—107°. When alcoholic sodium ethoxide is added to a solution of cyanomethazonic acid in absolute alcohol, sodium nitrite is precipitated, and benzylamine added to a solution of it in benzene gives rise to benzylamine nitrite.

The *compound*, $C_6H_4N_4O_2$, is produced when cyanomethazonic acid is heated with boiling water in a reflux apparatus during many hours, and also occurs as a bye-product in the preparation of that substance; it melts at 72°, and forms white crystals resembling ammonium chloride. It is insoluble in carbon bisulphide and petroleum, but dissolves readily in acetone, and sparingly in water, alcohol, ether and chloroform. Soda dissolves it readily when heated, but it is not thrown down from this solution by acids, these causing effervescence, and liberating hydrogen cyanide. Cold concentrated sulphuric acid dissolves the substance, generating heat in the process; oxalic acid is subsequently found in the solution.

M. O. F.

α-Hydroxylaminebutyric Acid. By ALFRED WERNER and R. FALCK (*Ber.*, 1896, **29**, 2654—2659. Compare Abstr., 1893, i, 501; 1895, i, 125, 521).—When ethylic α-bromobutyrate (1 mol.) and benzenyl-

amidoxime (1 mol.) are warmed together in presence of alkali (2 mols.), condensation takes place with production of derivatives of benzenylamidoximebutyric acid, namely, its potassium and ethylic salts and its esoanhydride. These are separable by means of alkali, which leaves the ethylic salt undissolved, and if hydrochloric acid be subsequently added to the alkaline liquid, the esoanhydride is precipitated, the acid itself dissolving in excess of hydrochloric acid.

Ethylic benzenylamidoximebutyrate, $NH_2{\cdot}CPh{:}N{\cdot}O{\cdot}CHEt{\cdot}COOEt$, is a white substance melting at 57°; it is readily soluble in alcohol, ether and benzene, but insoluble in water and light petroleum.

Benzenylamidoximebutyric acid, $NH_2{\cdot}CPh{:}N{\cdot}O{\cdot}CHEt{\cdot}COOH$, is most readily obtained by hydrolysis of the foregoing ethylic salt; it forms white crystals, melting at 81—82°, is very sparingly soluble in water, more readily in petroleum and benzene, and is readily soluble in alcohol and ether. The *hydrochloride*, $C_{11}H_{15}N_2O_3Cl$, is formed by the action of concentrated hydrochloric acid on the esonahydride at 100—120°; it separates from water in prismatic crystals, melting at 148°, and is readily soluble in water and alcohol, but insoluble in most organic media.

Benzenylamidoximebutyric anhydride, $CPh{\lessgtr}\begin{matrix}NH{\cdot}CO\\N\text{———}O\end{matrix}{>}CHEt$, crystallises in prisms melting at 106°, and is insoluble in cold water, but dissolves readily in alcohol, ether, and benzene.

Benzenylchloroximebutyric acid, $CPhCl{:}N{\cdot}O{\cdot}CHEt{\cdot}COOH$, is obtained by the action of sodium nitrite on the solution of the hydrochloride of the above acid, and crystallises in colourless needles or leaflets melting at 77°. It is practically insoluble in water, but dissolves readily in alcohol, ether, benzene, and acetic acid. The corresponding *benzenylbromoximebutyric acid*, $CPhBr{:}N{\cdot}O{\cdot}CHEt{\cdot}COOH$, melts at 68·5°. *Ethylbenzhydroximebutyric acid*,

$$OEt{\cdot}CPh{:}N{\cdot}O{\cdot}CHEt{\cdot}COOH,$$

is formed by the action of sodium ethoxide on the foregoing chloroderivative; it crystallises in colourless needles, melts at 72°, dissolves readily in alcohol, ether, and benzene, but is insoluble in water. *Methylbenzhydroximebuytric acid*, $OMe{\cdot}CPh{:}N{\cdot}O{\cdot}CHEt{\cdot}COOH$, melts at 68°.

The *hydrochloride* of hydroxylaminebutyric acid,

$$COOH{\cdot}CHEt{\cdot}O{\cdot}NH_2,HCl,$$

is made by evaporating to dryness on the water bath a solution of ethylbenzhydroximebutyric acid in dilute hydrochloric acid; it melts at 165·5°, crystallises from water, in which it is readily soluble, and is sparingly dissolved by alcohol. *α-Hydroxylaminebutyric acid*,

$$COOH{\cdot}CHEt{\cdot}ONH_2,$$

is prepared from its hydrochloride by the action of silver hydroxide, subsequent treatment with hydrogen sulphide serving to decompose the resulting silver salt; it is a white substance, readily soluble in water and in alcohol, but insoluble in ether and light petroleum; it melts at 156°.

A. L.

Solubilities of Salts of Caproic and of Œnanthylic Acids. By Emil Altschul (*Monatsh.*, 1896, **17**, 567—578. Compare Abstr.,

1895, ii, 7).—As the results of determinations of the solubilities of the calcium and silver salts of hexoic (caproic) and of heptoic (œnanthylic) acid do not agree with the generalisations which Lieben has found to exist among the salts of other fatty acids, the author has re-determined these solubilities.

Deszáthy's filtering apparatus was used, and the determinations were made both by the method of "cooling" and of "warming."

The solubility of silver hexoate agrees with the formula

$$L = 0{\cdot}07802 + 0{\cdot}0003335(t - 0{\cdot}5^\circ) + 0{\cdot}000040136(t - 0{\cdot}5^\circ)^2.$$

The solubility of calcium hexoate at temperatures between 0° and 47° agrees with the formula $L = 2{\cdot}713 - 0{\cdot}01627t + 0{\cdot}0001257t^2$; and for temperatures between 47° and 70·5° the expression $L = 2{\cdot}226 + 0{\cdot}02335(t - 47^\circ) - 0{\cdot}0001517(t - 47^\circ)^2$ holds good. The numbers obtained by the author for these two salts agree with those obtained by Keppich (Abstr., 1889, 122).

The numbers obtained in the case of silver heptoate fall far below those obtained by Landau for the same salt (Abstr., 1894, i, 226). The formula given is $L = 0{\cdot}04492 + 0{\cdot}0006416(t - 2^\circ) - 0{\cdot}00000957(t - 2^\circ)^2 + 0{\cdot}0000002905(t - 2^\circ)^3$. The solubility of calcium heptoate between 0·5° and 47·5° is $L = 0{\cdot}9015 — 0{\cdot}00199007(t - 0{\cdot}5^\circ) + 0{\cdot}000001702(t - 0{\cdot}5^\circ)^2$; and between 47·5° and 77·5°

$$L = 0{\cdot}7923 + 0{\cdot}0020102(t - 47{\cdot}5^\circ) + 0{\cdot}00002056(t - 47{\cdot}5^\circ)^2.$$

J. J. S.

Derivatives of Arachidic Acid. By MAX BACZEWSKI (*Monatsh.*, 1896, **17**, 528—546).—*α-Bromarachidic acid*, $C_{20}H_{39}BrO_2$ is obtained when arachidic acid is treated with bromine in presence of amorphous phosphorus; it forms white, silky crystals, melts at 62—64°, and dissolves readily in alcohol, ether, light petroleum and chloroform. The *ethylic* salt dissolves readily in ether, light petroleum and chloroform and crystallises in microscopic needles melting at 37—39°; the *methylic* salt has similar properties and melts at 33—35°. The *sodium* salt, $C_{20}H_{38}BrO_2Na$, *calcium*, *copper* and *silver* salts are described.

α-Iodarachidic acid, $C_{20}H_{39}IO_2$, is prepared by the action of potassium iodide on the foregoing acid; it crystallises in small, white prisms and melts at 70°; the *silver* salt is a yellow powder.

A small quantity of an unsaturated acid is formed when arachidic acid is heated with bromine and water in a sealed tube at 170°.

α-Hydroxyarachidic acid, $C_{20}H_{40}O_3$, is formed from α-bromarachidic acid when it is heated with alcoholic soda during 20 hours; it forms silky leaflets melting at 91—92°. The *ethylic* salt is soluble in alcohol, ether, etc., and crystallises in aggregations of needles melting at 62—66°; the *methylic* salt forms slender, white needles, and melts at 62—64°.

α-Ethoxyarachidic acid, $C_{22}H_{44}O_3$, is obtained by heating the hydroxy-acid with sodium ethoxide; it crystallises in slender needles, dissolves in the ordinary media and melts at 53—56°, its *ethylic* salt, $C_{24}H_{48}O_3$, crystallises in attenuated needles and melts at 35—37°; the *sodium*, *barium*, and *lead* salts are described.

α-Amidoarachidic acid, $C_{20}H_{41}NO_3$, results from the action of α-

bromarachidic acid on ammonia at 140°; it is very sparingly soluble in hot alcohol, more readily in hot acetic acid, but is insoluble in ether, petroleum, benzene, chloroform and strong hydrochloric acid; it darkens and melts at 212—214°, evolving gases, and the residue remains fluid at 40°. It is not identical with the acid obtained by Tassinari (Abstr., 1879, 307) on reducing nitroarachidic acid, as the former yields metallic salts whilst the latter does not; the *sodium* salt, $C_{20}H_{40}NO_2Na$, is a white, crystalline powder sparingly soluble in alcohol, whilst the *calcium* salt, $(C_{20}H_{40}NO_2)_2Ca$, is amorphous.

When α-bromarachidic acid is heated at 180°, with excess of aniline, during 7 hours, *α-anilidoarachidanilide*, $C_{32}H_{50}N_2O$, is obtained; it crystallises in amorphous grains melting at 82°, and is readily soluble in alcohol, benzene, petroleum, chloroform, and acetic acid, but is not dissolved by alkalis. If the temperature of the original mixture is maintained at 140° during 1 hour only, *α-anilidoarachidic acid*, $C_{26}H_{45}NO_2$, is produced. The latter dissolves sparingly in alcohol, readily in acetic acid and chloroform, but is insoluble in petroleum; it melts at 138—139°.

α-Cyanarachidic acid may be prepared by boiling an alcoholic solution of the bromo-acid with potassium cyanide during 5 days; it separates from alcohol as a white, crystalline powder, melts at 88°, and evolves gases at about 170°; when boiled with potash, it evolves ammonia and yields a mixture of two acids which may be separated by means of ether; the insoluble portion consists of *octodecylmalonamic acid*

$$C_{18}H_{37}\cdot CH(CONH_2)\cdot COOH,$$

which crystallises from acetic acid and melts with effervescence at 126°. The soluble fraction contains *octodecylmalonic acid*,

$$C_{18}H_{37}\cdot CH(COOH)_2.$$

The latter is finally crystallised from petroleum (whereby a more readily soluble substance melting at 70—80° is eliminated) and is then obtained in white, crystalline granules melting at 109—110°; it decomposes, evolving carbonic anhydride, at 124—170°, and the residue subsequently melts at 73°.

Arachidamide, $C_{20}H_{41}NO$, melts, as asserted by Fileti and Ponzio (compare Abstr., 1894, i, 13) at 108°. *Arachidanilide*, $C_{26}H_{45}NO$, may be obtained in a pure condition by heating arachidic acid and aniline together at 200°; it crystallises from alcohol in long, felted needles and melts at 96°. A. L.

Derivatives of Dimethylacrylic Acid. By BERTRAM PRENTICE (*Annalen*, 1896, **292**, 272—295. Compare Abstr., 1895, i, 17).—*Ethylic αβ-dibromisovalerate* is obtained by the action of bromine dissolved in carbon bisulphide on ethylic dimethacrylate (compare Ariff, *loc. cit.*, 16); it is a liquid of sp. gr. = 1·1652 at 17°/4°, having an agreeable odour of peppermint, and boils at 127—128° under a pressure of 30 mm.

Chlorhydroxyisovaleric acid, $OH\cdot CMe_2\cdot CHCl\cdot COOH$, is prepared from dimethacrylic acid by means of hypochlorous acid, and crystallises in colourless plates; the *calcium* and *barium* salts contain $2H_2O$, whilst the *cadmium*, *zinc*, and *copper* salts are anhydrous.

Chlorodimethacrylic acid, $CMe_2\colon CCl\cdot COOH$, is produced when concentrated sulphuric acid acts on chlorhydroxyisovaleric acid, and it crystallises from water in white needles melting at 85—86°; the *calcium* salt contains $4H_2O$, and crystallises in large, rhombohedral prisms, whilst the *strontium* salt, which also contains $4H_2O$, crystallises in needles and plates. The *barium* and *cadmium* salts are also crystalline, the *magnesium* salt contains $3\frac{1}{2}H_2O$, the *lead* salt $2H_2O$, and the *silver* salt crystallises in long, slender needles.

ββ-Dimethylglycidic acid, $O<\begin{matrix}CMe_2\\ | \\ CH\cdot COOH\end{matrix}$, is obtained from chlorhydroxyisovaleric acid by elimination of hydrogen chloride with alcoholic potash; although the acid has not yet been obtained in crystals, the *potassium* salt, containing $\frac{1}{2}H_2O$, forms colourless plates, and the *silver* salt crystallises from hot water in small plates.

1-*Phenyl*-3-*dimethyl*-5-*pyrazolidone*, $NPh<\begin{matrix}NH\cdot CMe_2\\ \quad | \\ CO—CH_2\end{matrix}$, is produced when dimethacrylic acid and phenylhydrazine are heated at 115° in the oil-bath, the temperature being subsequently raised to 175°; it crystallises in stellar aggregates of colourless needles, and melts at 74·5—75°. The *hydrochloride* forms microscopic needles. The *acetyl*-derivative melts at 104·5—105°, and crystallises in large, six-sided prisms; the *nitroso*-derivative is an unstable substance, and is very readily soluble in common solvents.

β-Phenylazoisovaleric acid, $NPh\colon N\cdot CMe_2\cdot CH_2\cdot COOH$, is formed when the foregoing substance is heated with baryta in a reflux apparatus; it crystallises from glacial acetic acid in long prisms, and melts at 57·5—58°. The *silver* salt crystallises from hot water in needles.

1-*Phenyl*-2 : 3 : 3-*trimethyl*-5-*pyrazolidone*, $NPh<\begin{matrix}NMe\cdot CMe_2\\ \quad | \\ CO—CH_2\end{matrix}$, is obtained from the pyrazolidone derivative by means of methylic iodide; the *hydrochloride* crystallises in needles. M. O. F.

General Synthetical Method for the Preparation of γδ-Unsaturated Acids.—By FRITZ FICHTER (*Ber.*, 1896, **29**, 2367—2372).—γδ-Unsaturated acids can readily be obtained by the distillation of δ-lactone-γ-carboxylic acids; this reaction is analogous to that used by Fittig in the preparation of βγ-unsaturated acids, namely by the distillation of γ-lactone-β-carboxylic acids (paraconic acids). The δ-lactone-γ-carboxylic acids are best obtained by the reduction of the corresponding dibasic ketonic acids or of their ethereal salts (compare Gantter, *Diss.*, 1878).

Ethylic acetylglutarate, $COOEt\cdot CHAc\cdot CH_2\cdot CH_2\cdot COOEt$, when reduced with aqueous alcohol and sodium amalgam, yields a *δ-caprolactone-γ-carboxylic acid*, $CH_2<\begin{matrix}CH(COOH)\cdot CHMe\\ CH_2——————CO\end{matrix}>O$; it forms a syrupy mass which, on drying at 120—125° and then cooling, becomes solid, it crystallises in small plates and melts at 107—108°. The acid readily reacts with water; on exposure to moist air, it is converted into a syrup consisting of a mixture of the δ-lactone-monocarboxylic acid

and the δ-hydroxydicarboxylic acid. (Compare Weidel, Abstr., 1891, 733.) No salts of the lactonic acid could be obtained, but salts of the hydroxydicarboxylic acid (5-hexanoloic 4-methyloic acid) were easily prepared. The *barium* and *calcium* salts are readily soluble in water, and on evaporation yield a friable mass, whilst the *silver* salt forms a white flocculent precipitate. The acid itself could not be isolated in a state of purity.

When a small quantity of δ-caprolactone-γ-carboxylic acid is distilled, the distillate contains a crystalline dibasic acid, which melts at 152° and is isomeric with the lactonic acid, and a second oily acid which is best separated by distillation in steam. The acid which thus passes over, after purification by means of its barium salt, boils at 206·5°. This *γδ-hexenic acid* is isomeric with hydrosorbic acid, but differs from it in the fact that it becomes crystalline when cooled to $-10°$ and the crystals then melt at 0°. Its *cadmium* salt is more readily soluble in hot water than in cold and crystallises in large, glistening, flat needles. Cadmium hydrosorbate, on the other hand, is much more sparingly soluble in hot than in cold water. The γδ-hexenic acid is not altered by boiling for 50 hours with a 20 per cent. solution of sodium hydroxide. Hydrosorbic acid when subjected to the same treatment yields αβ-hexenic acid and also β-hydroxycaproic acid (compare Fittig and Baker, Abstr., 1895, i, 206). The author has also reduced benzoylglutaric acid, and then distilled the resulting hydroxy-acid ; he finds that the method is a general one for the preparation of γδ-unsaturated acids.

J. J. S.

Thioglyoxylic (Ethanethiolic) Acid. By H. BRUNEL (*Bull. Soc. Chim.*, 1896 [3], **15**, 134).—By the action of a solution of sodium carbonate and sodium sulphide on dichloracetic acid, and subsequent treatment of the mixture with sulphuric acid, the author obtains *thioglyoxylic acid*, CHS·COOH, as a viscous substance, decomposing on distillation in a vacuum. It forms unstable lead and silver salts, and, on treatment with alcohol and hydrogen chloride, an *ethylic* salt, boiling at 61° under 36 mm. pressure. On boiling the aqueous solution of the acid with mercuric oxide, glyoxylic acid is produced.

M. W. T.

Transformation of Unsaturated α-Hydroxy Acids into the Isomeric γ-Ketonic Acids. By RUDOLPH FITTIG (*Ber.*, 1896, **29**, 2582—2584).—All the substances described by Tiemann and Biedermann (Abstr., 1892, 471) as derivatives of phenylhydroxycrotonic acid have been shown to be derived from benzoylpropionic acid (compare Abstr., 1895, i, 533), which was prepared from succinic anhydride and benzene in the presence of aluminium chloride. The real *α-hydroxy-γ-phenylcrotonic acid*, CHPh:CH·CH(OH)·COOH, can be obtained by saturating a cooled ethereal solution of cinnamaldehyde cyanhydrin with concentrated hydrochloric acid, and then allowing it to remain at the ordinary temperature until no more ammonium chloride separates. It melts at 137°, and also differs in its other properties from benzoylpropionic acid, $COPh{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$;

it is converted almost quantitatively into this acid, however, by boiling with 7 per cent. hydrochloric acid.

Pure crotonaldehyde cyanhydrin behaves in a similar manner although it contains no benzene residue. It yields *a-hydroxypentenoic acid*, CHMe:CH·CH(OH)·COOH, a syrup which takes up 2 atoms of bromine, and yields no phenylhydrazone. Its calcium salt is insoluble in alcohol; when this salt is boiled with excess of dilute hydrochloric acid, levulinic acid, $CMeO·CH_2·CH_2·COOH$, is produced, the calcium salt of which is insoluble in alcohol, and which yields a hydrazone.

It would appear, therefore, that acids of the type

R·CH:CH·CH(OH)·COOH

are in general transformed into isomeric acids of the type

$R·CO·CH_2·CH_2·COOH$

when they are boiled with dilute hydrochloric acid. C. F. B.

Volatility of Levulinic Acid. By MARCELLIN BERTHELOT and GUSTAVE ANDRÉ (*Compt. rend.*, 1896, **123**, 341—343).—Levulinic acid is very slightly volatile in steam, but when the dry compound is kept over quicklime or sulphuric acid, it gradually loses weight, the loss being greater in a vacuum than under ordinary pressure, and more rapid over sulphuric acid than over lime. The residue in either case, although crystalline, is partly liquid, and contains less carbon and more hydrogen than the original acid; it would seem that the levulinic acid tends to split up into two parts, the more volatile of which has the composition $4C_5H_8O_3 - H_2O$, whilst the residue seemingly contains dihydroxyvaleric acid. According to this result, levulinic acid is the first anhydride, lactone or olide of the dihydroxyvaleric acid. C. H. B.

Claisen's Condensation Method. By J. BOËSEKEN (*Rec. Trav. Chim.*, 1896, **15**, 161—164).—The ethereal salts of mono-, di- or tri-substituted acetic acids should react with ethylic acetate in the presence of sodium ethoxide in a manner analogous to the ordinary Claisen condensation. The author has made experiments with the ethylic salts of propionic, phenylacetic, isobutyric, and trimethylacetic acids in the presence of ethylic acetate and sodium ethoxide; but only with ethylic phenylacetate and ethylic propionate did any condensation take place.

The product formed from ethylic acetate and propionate in presence of sodium ethoxide is probably a mixture of ethylic propionylacetate, $CH_2Me·CO·CH_2·COOEt$, and ethylic methylacetoacetate, COMe·CHMe·COOEt, it is a colourless liquid which boils at 192°, and the yield is extremely poor. J. J. S.

Trithiodilactylic Acid. By JOHAN M. LOVÉN (*Zeits. physikal. Chem.*, 1896, **21**, 134—136).—By the interaction of hydrogen sulphide and pyruvic acid, a sulphur compound was obtained which was regarded as trithio-dilactylic acid, this view being supported by its conductivity (Abstr., 1894, 1, 325). The author has further determined the E.M.F. of chains containing the silver salt of the acid, and silver nitrate, and

obtained the values 0·157 and 0·171. If the compound contained mercaptan groups, this value should be much higher, so that the previous view of the constitution is confirmed. L. M. J.

Decomposition of Dibromosuccinic Acids with Water. By WILHELM C. LOSSEN and WALTHER RIEBENSAHM (*Annalen*, 1896, **292**, 295—317).—The authors' experiments lead them to the following conclusions.

Dibromosuccinic acids, when treated with 200 parts of boiling water, are decomposed in accordance with the equations

I. $C_4H_4Br_2O_4 = C_4H_3BrO_4 + HBr.$
II. $C_4H_4Br_2O_4 + H_2O = C_2H_4O + 2CO_2 + 2HBr.$
III. $C_4H_4Br_2O_4 + 2H_2O = C_4H_6O_6 + 2HBr.$

The change represented by I affects 50 per cent. of dibromosuccinic acid, only 20 per cent. of dibromisosuccinic acid being decomposed in this manner, more of the latter than of the former undergoing change according to II and III; both acids yield racemic and mesotartaric acids, racemic acid preponderating when dibromisosuccinic acid is used, whilst dibromosuccinic acid yields chiefly mesotartaric acid.

According to the statement of Fresenius, barium racemate separates from boiling solutions in anhydrous crystals, whilst at ordinary summer temperatures the salt contains $2\frac{1}{2}H_2O$. The authors have also obtained a salt containing $5H_2O$ from solutions at ordinary winter temperatures. Barium mesotartrate is usually described as a salt which dissolves readily in hot water, and becomes anhydrous at 100—110°; this, however, is erroneous, as the salt contains $1H_2O$ at 100°, and becomes anhydrous at 170°. M. O. F.

Malononitrile and some of its Derivatives. By B. C. HESSE (*Amer. Chem. J.*, 1896, **18**, 723—751. Compare Abstr., 1896, i, 458). —The malononitrile (m. p. 29°; b. p. 219—220°) used by the author was prepared by distilling dry cyanacetamide with an equal weight of phosphorus pentachloride. It is incidentally shown that dibromocyanacetamide and not the monobromo-derivative is the chief product of the interaction of cyanacetamide and bromine in cold aqueous solution (compare Nef, *Annalen*, 1894, **280**, 334). The action of bromine on the nitrile is complex, but both the monobromo- and dibromo-derivatives were obtained by adding the requisite weight of bromine to an aqueous solution of the nitrile.

Bromomalononitrile, $CHBr(CN)_2$, is a white, crystalline solid; it melts at 65—66°, and is slightly soluble in water and light petroleum, but dissolves readily in the ordinary organic solvents. *Dibromomalononitrile*, $CBr_2(CN)_2$, a white, crystalline substance, melts at 123·5—124°, and is easily soluble in alcohol, ether, and boiling chloroform, but less so in benzene and light petroleum. On pouring a cold aqueous solution of malononitrile (1 mol.) into a cold solution of ammoniacal silver nitrate (2 mols.), a mixture of mono- and di-silver malononitrile was obtained.

Diethylmalononitrile, $CEt_2(CN)_2$, was prepared both by heating a mixture of ethylic iodide (56 grams) and silver malononitrile (25

grams), and also by heating these substances with ether for 5 hours in a sealed tube at 100°. In both cases, the yields were low—15·6 per cent. and 6·4 per cent. of the theoretical quantities respectively, ethylic isocyanide and amorphous substances being formed at the same time. Diethylmalononitrile is a white, crystalline substance, which melts at 44°, and is insoluble in cold water, but soluble in hot water and in the ordinary organic solvents. (Compare next abstract.)

Dimethylmalononitrile, $CMe_2(CN)_2$, prepared similarly, is a white, crystalline solid melting at 32—32·5°, easily soluble in alcohol, ether, acetone and ethylic acetate, less soluble in chloroform, benzene and light petroleum, and insoluble in water. (Compare next abstract.)

The bearing of the formation of dialkylmalononitriles (accompanied by the formation of alkylic isocyanides), as above described, on the constitution of disilver malononitrile, is discussed, and the formula AgN:C:C:C:NAg is considered to be most probable. Attempts to prepare disodiomalononitrile by the interaction of sodium and malononitrile in ethereal solution with the addition of small quantities of alcohol, resulted in the formation of a substance which was apparently a mixture of the monosodium compound and sodium ethoxide. It reacts with alkylic iodides (see below) as though it contained both mono- and di-sodio-nitrile, and gave hydrocyanic acid with dilute acids. This fact is regarded as evidence that the metal is in direct combination with nitrogen. When this substance is heated with ethylic or methylic iodide, dimethyl- or diethyl-malononitrile is formed; in both cases hydrocyanic acid is also formed, and this is attributed to the decomposition of the monalkylmalononitrile. When ethylic chloroformate is added to an alcoholic solution of malononitrile containing one equivalent proportion of sodium ethoxide, a reaction occurs at once with formation of Haller's ethylic sodiodicyanacetate (Abstr., 1890, 1395) to the extent of 70 per cent. of the theoretical yield. Another substance yielding a yellowish precipitate with silver nitrate is also produced.

Methylic sodiodicyanacetate, prepared in similar manner, is soluble in ethylic acetate, and is precipitated from its alcoholic solution by benzene, light petroleum, chloroform and ether. When boiled with concentrated sodium hydroxide solution, no ammonia is formed, and it does not react with dilute (1 : 5) sulphuric acid. In its stability towards hydrolysing reagents, it resembles the corresponding ethylic salt.

The action of methylic iodide on a mixture of malononitrile and sodium methoxide in methylic alcohol solution gave, as the chief product, an oil boiling at 74—76° (22 mm.) having a fragrant, mint-like odour. Analysis pointed to the presence of 20 per cent. of dimethylmalononitrile with 80 per cent. of its imido-methyl ether, $CN\cdot CMe_2\cdot C(NH)\cdot OMe$; the existence of the latter was proved by treating the oil with dilute hydrochloric acid, when it underwent decomposition into methylic dimethylcyanacetate and ammonium chloride.

When ethylic alcohol and ethylic iodide were substituted for the corresponding methyl compounds in the above experiment, the products

obtained were diethylcyanacetamide and an oil consisting of diethylmalononitrile and its imido-ethyl ether. When this oil was dissolved in absolute ethylic alcohol containing some sodium ethoxide, and allowed to stand for 28 hours, almost the whole of the nitrile was converted into the imido-ether, a colourless mobile oil of mint-like odour; the action of aqueous hydrochloric acid changes this into ethylic diethylcyanacetate, a colourless oil of fragrant odour, boiling at 100—101° (14 mm.).

Diethylcyanacetamide, $CN{\cdot}CEt_2{\cdot}CO{\cdot}NH_2$, is formed in the above reaction, also in the preparation of diethylmalononitrile from the sodium salt and ethylic iodide in sealed tubes, and by boiling diethylmalononitrile with absolute alcohol containing 1·3 per cent. of sodium. In the last reaction, it is probable that the dialkyl amido-ether, $CN{\cdot}CEt_2{\cdot}C(OEt)_2{\cdot}NH_2$, is first formed, and that this at the boiling point of alcohol loses ethylic ether and forms the amide (compare Trans., 1896, 991). This crystallises in colourless plates melting at 120°, and is soluble in alcohol, ether and chloroform; less so in light petroleum and benzene.

Diethylcyanacetic acid, $CN{\cdot}CEt_2{\cdot}COOH$, was prepared (1) from the oil obtained in the reaction between ethylic iodide, malononitrile and sodium ethoxide, (2) from diethylmalononitrile, and (3) by heating diethylcyanacetamide in sealed tubes at 100° for 2 hours with concentrated hydrochloric acid. It was obtained as a colourless oil boiling at 162—164° (18 mm.), but this soon solidified to a white, hygroscopic, ice-like solid melting at 57°. The cyanogen group is very stable, being unaffected by heating with concentrated hydrochloric acid in a sealed tube for 1 hour at 120°. The *silver* salt crystallises from boiling water in glistening needles. On heating with concentrated hydrochloric acid in a sealed tube at 160° for 8 hours, diethylcyanacetic acid is quantitatively converted into diethylacetic acid, a fact which shows that in all those substances yielding diethylcyanacetic acid the two ethyl groups are attached to the same carbon atom. The author is of opinion that in the metallic derivatives of malononitrile the metal is directly linked to nitrogen, and discusses the mechanism of the changes resulting in the production of the dialkyl derivatives and of the monimido ethers. A. C. C.

Malononitrile Derivatives and their Reduction. By GIORGIO ERRERA and E. BERTÈ (*Gazzetta*, 1896, **26**, ii, 220—228).—The authors have prepared malononitrile derivatives of the constitution $CR_2(CN)_2$ and find them to be very stable substances which are not affected by light as are those having the constitution $CHR(CN)_2$ prepared by Henry (*Jahresber.*, 1889, 637).

Dibenzylmalononitrile, $C(CH_2Ph)_2(CN)_2$, may be prepared by the action of sodium on an alcoholic solution of malononitrile and benzylic chloride, but is best obtained by heating dibenzylcyanacetamide (Errera, Abstr., 1895, i, 528) with phosphoric anhydride at 170—180°; the product is extracted with water, and the residue crystallised from alcohol. It forms long, colourless laminæ melting at 130°, and is soluble in alcohol, but insoluble in water.

Dipropylmalononitrile, $CPr_2(CN)_2$, is prepared by heating dipropylcyanacetamide with phosphoric anhydride, and after extraction with water is crystallised from petroleum; it separates in large, colourless crystals melting at 46—47°, and boils at 223—225°. It is soluble in organic solvents but not in water.

Diethylmalononitrile, $CEt_2(CN)_2$, is prepared in a manner similar to the preceding, and is purified by distillation in a current of steam; it forms a colourless, crystalline mass melting at 44—45°, and boiling at 195—195·5°; its odour slightly resembles that of camphor.

Dimethylmalononitrile, $CMe_2(CN)_2$, resembles the preceding in appearance and odour; it sublimes in long needles melting at 31—32°, and boils at 162·5°. (Compare preceding abstract.)

Dibenzylmalononitrile in alcoholic solution is reduced by sodium; after adding water, acidifying and boiling off the alcohol, ether extracts dibenzylcyanacetamide and dibenzylacetamide from the aqueous solution, and on concentrating the latter, the hydrochloride of *β-dibenzylethylamine*, $CH(CH_2Ph)_2{\cdot}CH_2{\cdot}NH_2$, is deposited. The free base is a heavy liquid of alliaceous ammoniacal odour, and is insoluble in water; the *hydrochloride* crystallises in long, white needles, melting at 189—190° and is very soluble in alcohol, but only sparingly so in dilute hydrochloric acid. The *platinochloride* crystallises in lustrous yellow laminæ, melting and decomposing at 216—218°.

The subcutaneous injection of 0·30 gram of the hydrochloride is fatal to a rabbit, and on injecting the solution into the eye of a rabbit, local anæsthesia is produced. W. J. P.

Reduction of Dipropylmalononitrile. By GIORGIO ERRERA (*Gazzetta*, 1896, **26**, ii, 244—248. Compare preceding abstract).—Dipropylmalononitrile is reduced by boiling its alcoholic solution with sodium, and, on distilling the product in a current of steam, a solution of 4′-amino-4-methylheptane passes over and dipropylacetamide remains behind.

Dipropylacetamide, $CH(C_3H_7)_2{\cdot}CO{\cdot}NH_2$, crystallises in brilliant, white needles melting at 123—124° and is soluble in alcohol or ether.

4′-Amino-4-methylheptane, $CH(C_3H_7)_2{\cdot}CH_2{\cdot}NH_2$, is separated from the distillate obtained as above by evaporating it with hydrochloric acid; after adding potash, the base is extracted with ether. It is a colourless liquid of unpleasant, alliaceous odour, and boils at 167°; it is soluble in alcohol or ether, but only sparingly so in water or alkalis. It gives the isonitrile reaction. The *hydrochloride*, a white, waxy mass, is very soluble in water, alcohol, or ether; the *platinochloride* crystallises in yellow laminæ, melting and decomposing at 211°. The *benzoyl*-derivative, $CHPr_2{\cdot}CH_2{\cdot}NH{\cdot}COPh$, prepared by the action of benzoic chloride and potash on the base, crystallises in needles melting at 66—67°, and is very soluble in organic solvents, but insoluble in water. W. J. P.

Syntheses in the Adipic Acid Series. By CLEMENTE MONTEMARTINI (*Gazzetta*, 1896, **26**, ii, 259—290. Compare Abstr., 1896, i, 667).—On treating an alcoholic solution of ethylic malonate with sodium, and heating in a reflux apparatus with ethylic γ-chlorobutyrate

(Gabriel, Abstr., 1890, 1121), then adding water and extracting with ether, an oil is obtained which, by fractional distillation under reduced pressure, can be separated into ethylic malonate, ethylic γ-chlorobutyrate and an *ethylic butanetricarboxylate* having the constitution $CH(COOH)_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot COOH$. The ethylic salt is a colourless liquid boiling at 175—176° under 18 mm. pressure, and having the sp. gr. 1·0726 at 15°; it is readily hydrolysed by boiling with alcoholic potash, and after driving off the alcohol and acidifying with hydrochloric acid, the *tricarboxylic acid* can be extracted with ether. It crystallises in needles, melting and decomposing at 130°, and is soluble in ethylic acetate, but nearly insoluble in benzene; its *silver* salt, $Ag_3C_7H_7O_6$, forms a white, crystalline precipitate, and its *calcium* salt crystallises with $2H_2O$. When heated at 150°, the acid decomposes, giving adipic acid and carbonic anhydride.

On condensing ethylic methylmalonate and ethylic γ-chlorobutyrate with sodium in a similar manner, the *triethylic* salt, $C_{14}H_{24}O_6$, of a homologous pentanetricarboxylic acid is obtained as a colourless oil boiling at 181—183° under 12 mm. pressure; on hydrolysing the salt with alcoholic potash, the *pentanetricarboxylic acid* is obtained as an uncrystallisable syrup, which begins to lose carbonic anhydride at 105°. When distilled under reduced pressure, it yields a syrupy liquid, which contains a trace of adipic acid and partially crystallises over sulphuric acid. It is a mixture of a solid and a liquid acid, which may be partially separated by repeated crystallisation, and completely by heating with acetic chloride on the water bath, adding benzene and then cautiously extracting with water. On evaporating the benzene solution and taking up the residue with water, αβ-dimethylglutaric acid is obtained, whilst the aqueous solution yields α-methyladipic acid (Trans., 1895, 115).

αβ-Dimethylglutaric acid, $COOH \cdot CH_2 \cdot CHMe \cdot CHMe \cdot COOH$, is a liquid which boils at 220—224° under 24 mm. pressure, and yields succinic acid on boiling with chromic acid mixture. It may be synthesised by converting ethylic β-methyllevulinate into the corresponding nitrile by treatment with potassium cyanide and hydrochloric acid, and converting the nitrile into *ethylic α-hydroxy-αβ-dimethylglutarate* by hydrolysis with alcohol and hydrogen chloride: this ethylic salt is an oil which yields αβ-dimethylglutaric acid and glutaric acid on heating it with hydriodic acid. The *silver* salt of dimethylglutaric acid is a white, crystalline precipitate, sparingly soluble in hot water. The acid is converted into a liquid *anhydride* by treatment with acetic chloride, and partially by distillation under reduced pressure; it yields a viscid, uncrystallisable *anilide*, $C_{10}H_{17}NO_3$, when mixed with aniline in benzene solution.

The ethylic butanetricarboxylate, $C_{13}H_{22}O_6$, described above may be methylated by treating it first with sodium ethoxide and then with methylic iodide, whereby the *ethylic* salt,

$$CMe(COOEt)_2CH_2 \cdot CH_2 \cdot CH_2 \cdot COOEt,$$

of a homologous tricarboxylic acid is produced; this is a colourless

oil, boiling at 182—185° under 32 mm. pressure, and yields a solid *pentanetricarboxylic acid* when hydrolysed with alcoholic potash. The acid decomposes on distillation, yielding α-methyladipic acid, but no αβ-dimethylglutaric acid.

On condensing ethylic ethylmalonate with ethylic γ-chlorobutyrate, the *ethylic salt*, $CEt(COOEt)_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot COOEt$, of a tricarboxylic acid is obtained; it boils at 205—208° under 35 mm. pressure, and on hydrolysis with alcoholic potash yields a liquid *hexanetricarboxylic acid.* This when distilled in a vacuum gives a mixture of two isomeric acids, which may be separated by treating with acetic chloride; α-ethyladipic acid and α-ethyl-β-methylglutaric acid are thus obtained.

α-Ethyladipic acid, $COOH\cdot CHEt\cdot CH_2\cdot CH_2\cdot CH_2\cdot COOH$, boils at 225—226° under 20 mm. pressure, melts at 46—49°, and gives a very soluble *calcium* salt; it yields succinic acid when oxidised with chromic acid mixture, and when distilled in a vacuum with acetic chloride gives an oil which is insoluble in water, is volatile in a current of steam, and has an odour resembling that of mint. It is an *ethylketopentamethylene*, $\begin{array}{l} CO\text{——}CH_2 \\ | \\ CHEt\cdot CH_2 \end{array}\!\!>CH_2$, and is the product of decomposition of the anhydride. The ethylic salt described above, which boils at 205—208° under 35 mm. pressure, is readily methylated, yielding the *ethylic* salt, $C_{15}H_{16}O_6$, of a homologous acid; the *acid* obtained by hydrolysing it with alcoholic potash, yields α-ethyladipic acid when distilled under reduced pressure. W. J. P.

Ethylic Isoallylenetricarboxylate. By GUIDO GOLDSCHMIEDT and GUSTAV KNÖPFER (*Monatsh.*, 1896, **17**, 506—514).—Sodium (1 atom) is dissolved in absolute alcohol and added to a mixture of β-dibromacrylic acid (1 mol.) and ethylic malonate (1 mol.) and the whole is allowed to remain in ice during several days; the subsequent addition of water causes the precipitation of an oil, from which crystals of *ethylic isoallylenetricarboxylate*, $COOEt\cdot CH\!:\!C\!:\!C(COOEt)_2$, are deposited and are separated by filtration. The salt thus obtained is insoluble in water and in aqueous alkalis, sparingly soluble in ether, light petroleum and benzene, dissolves readily in acetic acid and melts at 107°; it crystallises from ether in colourless monoclinic prisms $a : b : c = 0{\cdot}70 : 1 : ?$. $\beta = 70{\cdot}5°$; its behaviour is not that of an acetylene derivative as it yields no precipitate with ammoniacal cuprous chloride, cupric nitrate, or mercuric chloride. A small quantity of the substance was hydrolysed with potash in a vessel connected with a washing bottle and two flasks containing ammoniacal silver nitrate and mercuric chloride respectively, a stream of air being led through the whole apparatus; no precipitate was produced in either of the solutions, and the alkaline residue, after acidification and extraction with ether, yielded a small quantity of a strongly acid syrup. Ethylic isoallylenetricarboxylate is not attacked by bromine, as would be the case were it an acetylene derivative. A. L.

Ethylic Deoxalate. By ANTON STEYRER and WALTHER SENG (*Monatsh.*, 1896, **17**, 613—635).—The authors have investigated ethylic

deoxalate which was first obtained by Löwig by the action of sodium on ethylic oxalate. They find that the best yield of the deoxalate is obtained when ethylic oxalate (3 mols.) is treated with sodium (5 atoms), in the form of 1·5 per cent. sodium amalgam, at a temperature between 5° and 20°. The mixture requires to be constantly shaken and kept at 10—15° for about an hour and a half. The product is extracted three times with anhydrous ether and the residue treated with dilute sulphuric acid, and not with water, as suggested by Löwig.

The acidified residue was found to contain oxalic acid and racemic acid, but no sugar (compare Löwig). The ethereal extract, if the above conditions be fulfilled, after evaporating the ether and keeping for several days, sets to a crystalline mass of ethylic deoxalate. If less than 5 atoms of sodium are used to 3 mols. of ethylic oxalate, the residue remains syrupy and contains alcohol, ethylic carbonate, and ethylic oxalate, besides ethylic deoxalate.

The deoxalate is slowly hydrolysed by cold water, more readily by hot, and is best recrystallised from a mixture of alcohol and ether. It may also be purified by distillation under diminished pressure, when it passes over at 156°—157° under a pressure of 2 mm. It forms colourless crystals, melts at 78° (corr.) and dissolves in cold water, yielding a perfectly neutral solution. On treatment with warm ammonia, it gives a yellow solution, which, in contact with the air turns reddish violet. Analyses, and also the estimation of ethyl groups by Zeisel's method, agree with the formula $C_5H_3Et_3O_8$.

The vapour density as determined by Hofmann's method shows that complete dissociation takes place at 180—210°.

Phenylhydrazine reacts with ethylic deoxalate to form the *ethylic* salt of E. Fischer's phenylhydrazineglyoxylic acid. This crystallises from aqueous alcohol in glistening, yellow plates, and melts at 127°. Hydroxylamine, on the other hand, yields glycollic acid and the *oxime of ethylic mesoxalate*—which is identical with Conrad and Bischoff's ethylic isonitrosomalonate (Abstr., 1882, 39). Other substances are probably formed at the same time. J. J. S.

Action of Formaldehyde on Carbamide. By CARL GOLDSCHMIDT (*Ber.*, 1896, **29**, 2438—2439). When formaldehyde is added to a solution of carbamide in dilute hydrochloric acid, a granular precipitate is produced which does not dissolve in any of the usual solvents. This substance is formed by the reaction of 2 molecules of carbamide with 3 of the aldehyde, and has the empirical formula $C_5H_{10}N_4O_3$. It is decomposed by strong acids but is not affected by alkalis. A. H.

Ammoniacal Fermentation of Uric Acid. By FAUSTO SESTINI and LEONE SESTINI (*Gazzetta*, 1896, **26**, ii, 92).—In connection with the recent work of Gérard (*Compt. rend.*, 1896, **122**, 1019), the authors point out that they were the first to study, chemically and bacteriologically, the fermentation of uric acid (Abstr., 1890, 1399).

W. J. P.

Action of Alkali Hypobromites on Succinodiamide. By W. van Dam (*Rec. Trav. Chim.*, 1896, **15**, 101—106).—The author has obtained succinodibromdiamide, $(CH_2{\cdot}CO{\cdot}NHBr)_2$ or

$$CH_2{\cdot}CO{\cdot}NBr_2,CH_2{\cdot}CO{\cdot}NH_2,$$

by a method slightly different from that given by van Ligne. Finely powdered succinamide was treated with the theoretical quantity of potassium hypobromite solution. The mixture was cooled and constantly stirred until it set to a pasty mass, which was then poured into 10 per cent. acetic acid. The bromamide was collected, well washed with ice-cold water, and then dried over sulphuric acid and potash.

When the succinodibromodiamide is treated with barium hydroxide solution first in the cold and then at 30—40°, it yields β-lactylcarbamide (compare Lengfeld and Stieglitz, Abstr., 1893, i, 632). The same compound can be obtained directly from succinodiamide by the action of a mixture of potassium hypobromite and hydroxide.

J. J. S.

Action of Alkali Hypochlorites and Hypobromites on Amides. By Sebastiaan Hoogewerff and Willem Arne van Dorp (*Rec. Trav. Chim.*, 1896, **15**, 107—115).—A historical survey of the work done by the authors and others on the action of alkali hypochlorites and hypobromites on acid amides. Compare Abstr., 1887, 245; 1888, 1194; 1889, 981; 1891, 196, 1216. Lengfeld and Stieglitz (Abstr., 1893, i, 310, 631; 1894, i, 415).

The authors show that part of the work done by Weidel and Roithner (Abstr., 1896, i, 470) has been previously published by themselves.

J. J. S.

Oximamidoxalic Acid and Hydroxyoxamide. By Arnold F. Holleman (*Rec. Trav. Chim.*, 1896, **15**, 148—156).—Schiff and Monsacchi have claimed that the compound described by them (Abstr., 1896, i, 209) as hydroxyoxamide, $NH_2{\cdot}CO{\cdot}CO{\cdot}NH{\cdot}OH$, is identical with the compound previously described (Abstr., 1894, i, 571) as oximamidoxalic acid, $NH_2{\cdot}C(NOH){\cdot}COOH$.

It is now pointed out that the compounds cannot be identical for the following reasons.

Schiff and Monsacchi's compound is coloured brownish-red by ferric chloride. It yields an acetyl derivative (m. p. 178°), and a benzoyl derivative (m. p. 157°) which easily crystallises.

Holleman's compound is coloured reddish-violet by ferric chloride. When heated with acetic acid and acetic anhydride, it yields no acetyl derivative, but is decomposed yielding cyanamide, but it yields an unstable benzoyl derivative, which is decomposed by hot alcohol.

The author thinks that Schiff and Monsacchi's compound has more the properties of $NH_2{\cdot}C(NOH){\cdot}COOH$ than of $NH_2{\cdot}CO{\cdot}CO{\cdot}NH{\cdot}OH$; thus it is not readily oxidised, whereas all substituted hydroxylamines are oxidised with the greatest ease. Its acetyl and benzoyl derivatives have fairly strong acid properties. The formula $NH_2{\cdot}C(NOH){\cdot}COOH$

also accounts for the fact that oxalic acid, ammonia and hydroxylamine are obtained when the compound is heated with hydrochloric acid on the water bath.

The author still retains the same constitution for his own substance, and as the possibility of the two substances being polymerides has been proved untenable by molecular weight determinations, they are probably stereoisomeric, as represented by the formulæ

$$\textit{syn}\ \begin{matrix} COOH\cdot C\cdot NH_2 \\ \Vert \\ HO\cdot N \end{matrix} \text{ and } \begin{matrix} COOH\cdot C\cdot NH_2 \\ \Vert \\ N\cdot OH \end{matrix}\ \textit{anti}.$$

The author gives the syn-formula to his own compound since it more readily accounts for the formation of cyanamide by the action of acetic anhydride (*loc. cit.*). The anti-configuration is given to Schiff and Monsacchi's compound as this more readily accounts for the formation of carbonic anhydride and carbamide when heated.

J. J. S.

Malic Derivatives of Aliphatic Amines. By ARNALDO PIUTTI and ERCOLE GIUSTINIANI. (*Gazzetta*, 1896, **26**, i, 431—440).—Körner and Menozzi (Abstr., 1895, i, 591), having prepared a methylfumaramic acid melting at 208°, by the action of methylic iodide and potash on dimethylasparagine, stated that the substance melting at 149° which Giustiniani obtained (Abstr., 1892, 821) by the action of alkali on the methylfumarimide prepared by distilling methylamine hydrogen malate cannot also be a methylfumaramic acid. The explanation of the disagreement is now given.

On heating ethylic hydrogen fumarate with absolute alcohol and dry methylamine for 3 hours at 110°, ethylic hydrogen methylaspartate is obtained instead of a synthetical methylfumaramic acid.

On mixing a benzene solution of malic anhydride with the equivalent quantity of an absolute alcoholic solution of methylamine, heat is developed and Giustiniani's acid melting at 149° crystallises out; on heating on the water bath with potash until all the methylamine is driven off, and then acidifying with hydrochloric acid, fumaric acid separates, but if the hydrolysis be performed with baryta, and the liquid acidified with sulphuric acid, malic acid is obtained. The acid melting at 149° decomposes above its melting point, yielding the so-called methylfumarimide melting at 90—92°.

It is consequently evident that the acid melting at 149° is *methylmalamic acid* and the imide melting at 90—92° is *methylmalimide*. Similarly, it is shown that Giustiniani's ethylfumaramic and benzylfumaramic acids are really malic derivatives, for when hydrolysed with baryta they yield malic acids; further, the corresponding imides melting at 45·5° and 67·5° must be regarded as ethylmalimide and benzylmalimide respectively.

The three malamic acids have the normal molecular weights by the ebullioscopic or cryoscopic method.

W. J. P.

Coal tar Thioxen [Dimethylthiophen]. By KARL KEISER (*Ber.*, 1896, **29**, 2560—2564).—Experiments were made with the view of

ascertaining whether the dimethylthiophen of coal tar is, like coal tar xylene, a mixture of different isomerides.

For this purpose, the crude oil was treated with bromine and the product distilled in a current of steam, when the xylenes first passed over, being followed by the bromo-compound, which sank to the bottom of the receiver. By subsequently fractionating this, *bromodimethylthiophen*, C_4SHMe_2Br, was obtained as a heavy, colourless oil boiling at 204—207°. On sulphonating this compound by Tohl's method, eliminating the bromine with sodium amalgam, converting the sulphonic acid into the chloride, and treating this with excess of ammonium carbonate, the mixed dimethylthiophensulphonamides, $C_4SHMe_2{\cdot}SO_2{\cdot}NH_2$, were obtained. From this, by fractional recrystallisation, the following compounds were isolated: (1) Fine needles, melting at 264°; (2) white, glistening needles, melting at 258°; (3) glistening prisms, melting at 225°; and (4) small needles, melting at 135°. The last compound was found to be identical with the sulphonamide of synthetically prepared 2 : 5 dimethylthiophen.

J. F. T.

Action of Aluminium Chloride on Benzene containing Thiophen. By EYVIND BOEDTKER (*Compt. rend.*, 1896, **123**, 310—311).—When ordinary crystallisable benzene is boiled with aluminium chloride, hydrogen sulphide is liberated, and the thiophen is decomposed, one of the products being a brown liquid with a green fluorescence; this boils above 300°, and contains traces of sulphur, but does not give the thiophen reaction. It is probable that the thiophen residue after elimination of sulphur combines with the residues of 2 molecules of benzene from which hydrogen has been eliminated. A condensed thiophen may be formed at the same time, as Hauer has supposed.

C. H. B.

Synthesis of Homocyclic Compounds. By ENRICO RIMINI (*Gazzetta*, 1896, **26**, ii, 325—380).—Ethylic acetonedicarboxylate and ethylic oxalate readily condense when dissolved in sodium ethoxide solution; when the insoluble sodium salt deposited is washed with ether and acidified, a substance which crystallises in small, white needles decomposing at 140—156° is obtained. It is probably *diethylic triketopentamethylene*-1 : 3-*dicarboxylate*, $COOEt{\cdot}CH{<}\begin{matrix}CO{\cdot}CH{\cdot}COOEt\\ \quad\ |\\ CO{\cdot}CO\end{matrix}$; when treated with hydroxylamine in alkaline solution, it yields, not a trioxime, but a *substance* of the composition $C_9H_{13}NO_9$.

On heating diethylic acetonedicarboxylate with ethylic malonate and sodium ethoxide, condensation occurs, and a substance is obtained which crystallises in beautiful, yellow pyramids melting at 100—101°; it is most probably *diethylic triketohexamethylene*-1 : 3-*dicarboxylate*, $CO{<}\begin{matrix}CH(COOEt){\cdot}CO\\ CH_2\text{———}CO\end{matrix}{>}CH{\cdot}COOEt$.

If the product left on distilling off the solvent from an alcoholic solution of ethylic acetonedicarboxylate, ethylic succinate and sodium ethoxide, is suitably treated, it yields ethylic succinylsuccinate, a

white, crystalline *substance* of the composition $C_8H_{10}O_4$, which melts at 98°, and an *acid*, $C_7H_6O_4$, which is obtained as a red powder melting at 186—187°. W. J. P.

Action of an Alkali Sulphite on Metadinitrobenzene. By RUDOLF NIETZKI and G. HELBACH (*Ber.*, 1896, **29**, 2448—2450).—When metadinitrobenzene is heated with sodium sulphite solution, it is converted into *nitranilinesulphonic acid* $[NH_2 : NO_2 : SO_3H = 4 : 2 : 1]$ which is very sparingly soluble in hot water, and crystallises in almost colourless, microscopic needles. Dilute sulphuric acid at 180° converts it into metanitraniline and sulphuric acid. The *potassium salt* crystallises in yellow quadratic plates. Nitrous acid converts the acid into an almost insoluble diazo-salt, and this, on boiling with alcohol yields a nitrosulphonic acid, which is converted by reduction into orthoanilinesulphonic acid. Since the nitranilinesulphonic acid is identical with that obtained by the reduction of dinitrobenzenesulphonic acid $[(NO_2)_2 : SO_3H = 4 : 2 : 1]$, it follows that it has the constitution assigned to it above. It is not, however, identical with the acid which was obtained by Pohl and Hartung (*Annalen*, **205**, 102) by the direct sulphonation of metanitraniline. On reduction, the metanitranilinesulphonic acid is converted into *metaphenylenediaminesulphonic acid*, which crystallises in colourless rhombic tablets and is converted by nitrous acid into a colouring matter of the phenylene-brown series. The corresponding *nitrohydrazinesulphonic acid* and its *hydrochloride* have also been prepared as well as *3-nitrophenol-4-sulphonic acid*, the *potassium salt* of which crystallises in yellow plates. A. H.

Preparation of Phenylacetylene. By ARNOLD F. HOLLEMAN (*Rec. Trav. Chim.*, 1896, **15**, 157—158. Compare Abstr., 1888, 261).—Phenylacetylene is best obtained by gently distilling phenylpropiolic acid with an excess of aniline, and pouring the distillate into dilute hydrochloric acid, when the phenylacetylene separates in an oily form, and may be extracted with ether; the yield is extremely good. J. J. S.

Solid Solutions of Phenol in Benzene. By FELICE GARELLI (*Gazzetta*, 1896, **26**, ii, 107—119).—The author has previously observed that phenol depresses the freezing point of benzene anomalously (Abstr., 1894, i, 157); in order to determine whether this is due to the formation of a solid solution of phenol in the freezing benzene, test experiments were made by Küster's method. Phenol and benzil were dissolved together in benzene, and the solution cooled as in molecular weight determinations by the cryoscopic method; the solid deposited was then separated and analysed. The quantity of phenol found in the frozen benzene was always greater than that of the benzil, so that the anomalous depression of the freezing point of benzene by phenol may be attributed to the formation of a solid solution of phenol in benzene; as the benzene solution is made more concentrated, the percentage of phenol in the solid which separates decreases continuously with the increase of the concentration, and this the author believes to be due to the fact that such solutions congeal at a lower temperature,

This point is of interest in connection with the distribution of a dissolved substance between two solvents in contact; if the phenol has the same molecular weight both in the liquid and solid benzene solution, the distribution of the phenol between the two kinds of solution should be independent of the concentration. Experiment shows, however, that the coefficient of distribution is much affected by change of temperature, and if benzene solutions of phenol be caused to freeze at a lower temperature by the addition of benzil, the proportion of the total phenol found in the solid solution is less than it would otherwise be. W. J. P.

Action of Sodium Sulphide on 1:4-Chloronitrobenzene. By FRIEDRICH KEHRMANN and EDUARD BAUER (*Ber.*, 1896, **29**, 2362—2367).—When the solution obtained by treating 1:4-chloronitrobenzene (1 mol.) with a cold alcoholic solution of sodium sulphide (1·5 mol.) is poured into water, the sodium salt of nitrothiophenol remains in solution, whilst a yellow, crystalline mass separates. Boiling dilute hydrochloric acid extracts *nitramidophenylic sulphide* from the solid mixture. It can be precipitated by ammonia and recrystallised from benzene, when it forms extremely long, orange-coloured prisms with a bluish glance. It melts at 143°, is insoluble in water, but is readily soluble in all organic solvents, and has the constitution

$$NO_2{\cdot}C_6H_4{\cdot}S{\cdot}C_6H_4{\cdot}NH_2\ [4:1:4].$$

Its *hydrochloride* crystallises in glistening, white needles, which are decomposed by water. On treatment with acetic anhydride, the base is converted into an *acetyl* derivative, which melts at 193°; and on reduction with stannous chloride, it yields Merz and Weith's thioaniline, which Nietzki and Bothof (Abstr., 1895, i, 132), have shown to be paradiamidophenylic sulphide.

An alcoholic solution of the nitroamido-compound on treatment with concentrated sodium nitrite solution yields *paranitrophenylic sulphide*, $Ph{\cdot}S{\cdot}C_6H_4{\cdot}NO_2$, which crystallises in pale yellow, transparent prisms and melts at 55°. On reduction with stannous chloride this nitro-compound yields *paramidophenylic sulphide* which melts at 93°; its *acetyl* derivative melting at 146°. Nietzki and Bothof's paradinitrophenylic sulphide (*loc. cit.*) on reduction with ammonium sulphide gives the above-mentioned nitroamino-base.

The residue left on extracting the yellow, crystalline mass with dilute hydrochloric acid yields, after several crystallisations from benzene, *paradichlorazoxybenzene*, which crystallises in colourless prisms and melts at 155° (compare Laubenheimer, *Ber.*, 8, 1626).

If a larger quantity of sodium sulphide (2 mols.) is used, the chief products are, besides nitrothiophenol, thioaniline, parachloraniline, and the azoxy-compound. J. J. S.

Migration of an Iodine Atom in Anisoïl and Phenetoïl Derivatives. II. By FRÉDÉRIC REVERDIN (*Ber.*, 1896, **29**, 2595—2599. Compare Abstr., 1896, i, 475).—Red 4 : 3-*iodonitranisoïl*, melting at 62°, was prepared by the action of potassium iodide on the diazo-compound from 3 : 4-nitranisidine; this amine was obtained by

hydrolysing 3 : 4-*nitracetanisidide*, a yellow substance, melting at 117°, which is formed when 4-acetanisidide is boiled with 11 per cent. nitric acid.

Derivatives of phenetoïl were also experimented with; they were prepared in the same way as the analogous anisoïl derivatives already examined. 2-*Iodophenetoïl* boils at 245° under 735·5 mm. pressure, and yields yellow 2 : 4-*iodonitrophenetoïl*, melting at 96°. This can be reduced to 2 : 4-*iodophenetidine*, the yellow *picrate* of which begins to decompose at 180°, whilst the *thiocarbamide*, *acetylderivative*, and condensation product with 1 : 2 : 4-chlorodinitrobenzene melt at 163°, 146°, and 172° respectively; the base itself, by means of the diazo-reaction, can be made to yield 2 : 4-*diiodophenetoïl*, which melts at 51°. 4-*Iodophenetoïl* melts at 29°, and boils at 249—250° under 729 mm. pressure; when nitrated, it yields the 2 : 4-iodonitro-compound mentioned above, the iodine atom having migrated to the 2 position.

4-Brom- and 4-chlor-anisoïl behave normally when nitrated, yielding compounds isomeric, and not identical, with those obtained by the nitration of 2-brom- and 2-chlor-anisoïl; no migration of the iodine atom takes place. 4-*Chloro-2-nitranisoïl* is apparently described for the first time; it is yellowish, and melts at 98·5°.

C. F. B.

Xylenolbromethylic Ether. By GEORG M. J. SCHRADER (*Ber.*, 1896, **29**, 2399—2403).—*a-Metaxylylic bromethylic ether*,

$$C_6H_3Me_2 \cdot O \cdot CH_2 \cdot CH_2Br,$$

[$Me_2 : O = 1 : 3 : 4$] is formed when ethylene bromide is boiled with an alcoholic solution of sodium ethoxide and 1 : 3 : 4-xylenol, and is a slightly brownish oil, which boils at 263—265°. It readily reacts with potassium phthalimide to form 1 : 3 : 4-*xylenoxyethylphthalimide*, $C_6H_3Me_2 \cdot O \cdot CH_2 \cdot CH_2 \cdot N \colon (CO)_2 \colon C_6H_4$, which crystallises in long, yellowish-white needles, melting at 113—114°. This compound cannot be directly used for the preparation of xylenoxyethylamine since the latter is decomposed by hydrochloric acid at the temperature required for the hydrolysis. It is therefore converted into 1 : 3 : 4-*xylenoxyethylphthalamic acid*, $C_6H_3Me_2 \cdot O \cdot C_2H_4 \cdot NH \cdot C_6H_4 \cdot COOH$, which crystallises in fascicular groups of needles, melting at 130—131°. When this is heated with hydrochloric acid on the water bath, it yields 1 : 3 : 4-*xylenoxyethylamine hydrochloride*, as a yellowish-white mass which has not been obtained pure. The free *base* is a strongly alkaline liquid, which boils at 249—250°. The *picrate* melts at 182—183°, and the *platinochloride* melts and decomposes at 211°. 1 : 3 : 4-*Xylenoxyethylbenzamide*, $C_{10}H_{13}O \cdot NHBz$, crystallises in slender needles, melting at 117—118°. *a-Metaxylenoxyethylacetamide* forms long, white needles, melting at 70—71°. *a-Metaxylenoxyethylcarbamide* crystallises in plates and melts at 132—133°. 1 : 3 : 4-Xylylic bromethylic ether is converted by aniline into 1 : 3 : 4-*xylenoxyethylaniline*,

$$C_6H_3Me_2 \cdot O \cdot C_2H_4 \cdot NHPh\ ;$$

this is an oily basic liquid, the *hydrochloride* of which crystallises in colourless plates and melts at 183—184°. Ammonia converts the

ether into 1 : 3 : 4-xylenoxyethylamine. Alcoholic potash reacts with the ether to form 1 : 3 : *4-xylenoxyethylic ether*, $C_8H_9 \cdot O \cdot C_2H_4 \cdot OEt$, which boils at 250—253°. Sodium ethoxide converts the brom-ether into 1 : 3 : *4-xylylic methylic ethylenic ether*, boiling at 245—247°, whilst sodium phenoxide forms the corresponding *phenylic 1 : 3 : 4-xylylic ethylenic ether*, which crystallises in flat prisms, melting at 76—77°. Potassium cyanide acts on the brom-ether as an alkali, yielding as final product *di-1 : 3 : 4-xylylic ethylenic ether*, $C_2H_4(O \cdot C_8H_9)_2$, the reaction being similar to that which it undergoes with cresol bromethylic ether. A. H.

Derivatives of Trichlorodinitrobenzene. By C. Loring Jackson and W. R. Lamar (*Amer. Chem. J.*, 1896, **18**, 664—685. Compare Abstr., 1891, 1024).—Trichlorodinitrobenzene (m. p. 129·5°, Abstr., 1887, 136) was prepared by nitrating 1 : 3 : 5-trichlorobenzene which is obtainable in quantity, through the diazo-reaction, from 2 : 4 : 6-trichloraniline prepared according to the directions of V. Meyer and Sudborough (*Ber.*, 1894, **27**, 3151). When heated with aniline, it yields trianilidodinitrobenzene (Abstr., 1890, 247).

5-Chlorodinitroresorcinol diethyl ether, $C_6HCl(OEt)_2(NO_2)_2$, is formed by adding an alcoholic solution of sodium ethoxide to a solution of 1 : 3 : 5 : 2 : 4-trichlorodinitrobenzene in a mixture of benzene and alcohol. It crystallises in yellowish-white prisms with square ends, melts at 160°, and dissolves in acetone, benzene, and chloroform, but only slightly in other solvents. When the reaction between sodium ethoxide and trichlordinitrobenzene is allowed to proceed at a higher temperature than that to which the heat of the reaction raises the solvents, *dinitrophloroglucinol triethyl ether*, $C_6H(OEt)_3(NO_2)_2$, is obtained; this crystallises in yellowish prisms terminated at each end by two planes at an obtuse angle to each other, melts at 104—105° and dissolves in hot alcohol or benzene, glacial acetic acid, chloroform and ether, but only sparingly in carbon bisulphide, and not at all in light petroleum and water; it becomes brown on exposure to the air. *Dinitrophloroglucinol diethyl ether*, $C_6H(OEt)_2(NO_2)_2 \cdot OH$, is formed together with the triethyl ether, and is separated from it by treating the product of the reaction with water, when the sodium salt of the diethyl ether dissolves; it crystallises in yellowish-white needles, melts at 166°, and sublimes; most solvents dissolve it, with the exception of light petroleum and cold water. The *sodium* salt dissolves in water, forming a dark orange-red, neutral solution which, when concentrated, yields a bright yellow, gelatinous precipitate with salts of calcium, strontium and barium, salmon-coloured flocks with ferric chloride and yellow flocks with lead acetate and with mercuric chloride.

Ethylic 3 : 5-dichlorodinitrophenylmalonate,

$$C_6H(NO_2)_2Cl_2 \cdot CH(COOEt)_2,$$

is prepared by mixing a solution of trichlorodinitrobenzene (1 mol.) in benzene with one of ethylic sodiomalonate (3 mols.) in alcohol, leaving the mixture at the ordinary temperature for 20 hours, and then pouring it into dilute sulphuric acid; the separated benzene is mixed with hot alcohol, when the new compound separates as the solvent cools.

It crystallises in white, thick, narrow plates terminated by two planes at an acute angle to each other; it melts at 101°, and is dissolved by most solvents except water. The *nitrite*,

$$C_6H(NO_2)_2Cl_2\cdot C(NO_2)(COOEt)_2$$

(compare Abstr., 1892, 1217), is formed when the ethylic salt is heated on the water bath with nitric acid (sp. gr. 1·38) for 5 minutes; it crystallises in white crystals, has no definite melting point, and dissolves in most solvents other than light petroleum and water.

3 : 5-*Dichlorodinitrophenylacetic acid*, $C_6H(NO_2)_2Cl_2\cdot CH_2\cdot COOH$, is prepared by boiling ethylic dichlorodinitrophenylmalonate with sulphuric acid (sp. gr. 1·44) in a reflux apparatus. It crystallises in yellowish-white needles, melts at 140°, and dissolves in glacial acetic acid, acetone, benzene, chloroform, ether, and in water containing sulphuric acid, but not in carbon bisulphide or light petroleum; in aqueous soda, it dissolves with a transitory crimson colour (for similar colour changes compare Abstr., 1896, i, 147, 214). The *sodium* salt forms pale yellow crystals; its aqueous solution is neutral, and gives a white flocculent precipitate with ferric chloride, a greenish-blue precipitate with cupric sulphate, a white, curdy precipitate with lead acetate, and a bluish-white precipitate with silver nitrate. The *ethylic* salt is easily obtained by boiling the acid with alcohol, evaporating, extracting with hot dilute sulphuric acid, and crystallising the residue first from light petroleum and then from alcohol. It crystallises in long, white needles, melts at 67—68°, and dissolves best in alcohol and hot light petroleum. A. G. B.

Derivatives of Veratrole. By AUSONIO DE GASPARI (*Gazzetta*, 1896, **26**, ii, 230—236).—*Monobromoveratrole*, $C_6H_3Br(OMe)_2$, may be prepared by aspirating air containing bromine vapour through a cooled acetic acid solution of veratrole; it is a colourless, highly refractive oil of pleasant odour boiling at 254·5—256° (compare Brüggemann, Abstr., 1896, i, 356). It is readily nitrated by dilute or fuming nitric acid, giving a *bromonitroveratrole*, $C_6H_2Br(OMe)_2\cdot NO_2$, which crystallises in yellow needles melting at 124·5—125°; it is volatile in a current of steam and may be sublimed, but partially decomposes with deflagration. *Bromodinitroveratrole*,

$$C_6HBr(OMe)_2(NO_2)_2,$$

is obtained by treating bromoveratrole with a mixture of sulphuric and fuming nitric acids; it is volatile in a current of steam, and crystallises in yellow needles melting at 113—114°. No trinitro-derivative could be prepared.

A *veratrolesulphonic acid*, $C_6H_3(OMe)_2\cdot HSO_3$, is obtained on heating a solution of veratrole in concentrated sulphuric acid on the water bath; the *barium* salt crystallises with $3H_2O$ in orthorhombic laminæ, loses its water of crystallisation at 140°, and begins to decompose at 145°. The *lead* salt crystallises with $3H_2O$ in pearly orthorhombic laminæ, and is very soluble in water; it becomes anhydrous at 135°. The free acid is volatile in a current of steam, crystallises with $2H_2O$ in laminæ or needles, decomposes at 100° without melting, and effervesces in a vacuum.

On heating the anhydrous sodium or barium salt with phosphorus pentachloride, an oily *sulphochloride* is obtained, which, when treated with ammonia, yields *veratrolesulphonamide*, $C_6H_3(OMe)_2\cdot SO_2\cdot NH_2$; this crystallises with $2H_2O$ in colourless needles, melting at 136·5—137·5°, and is very soluble in water. The *sulphonanilide*,

$$C_6H_3(OMe)_2\cdot SO_2\cdot NHPh,$$

crystallises with $2H_2O$ in long, white needles, melting at 130·5—131·5°; the sulphonamide yields an *acetyl*-derivative, $C_6H_3(OMe)_2\cdot SO_2\cdot NHAc$, which crystallises in thin needles melting at 140—141°.

W. J. P.

Cholesterol, IV. By JULIUS MAUTHNER and WILHELM SUIDA (*Monatsh.*, 1896, **17**, 579—603).—20 grams of dry cholesterol is dissolved in 1—1·5 litres of glacial acetic acid, and the solution quickly poured into a warm solution of 21 grams of chromic anhydride in ½—1 litre of acetic acid. After pouring into dilute sodium chloride solution, the mass is extracted with ether and the ethereal solution freed from acid substances by shaking with potash. On evaporating the ether, a honey-like mass is left, which gradually deposits a mass of crystals, consisting of three substances; two of these were removed by benzene, and the third—oxycholestendiol—remained behind. The benzene solution was evaporated and the residue fractionally crystallised, first from a small quantity of absolute alcohol, when oxycholestenone separated out in large glistening plates, and finally from dilute alcohol when α-oxycholestenol was obtained.

α-oxycholestenol, $C_{27}H_{42}O_2$, crystallises in colourless needles, melts at 180°, and is readily soluble in all organic solvents. It does not give the typical cholestol reaction, and does not react with phenylhydrazine. It apparently contains one hydroxyl group, as it yields a *monacetyl*-derivative which melts at 101—102°. On careful oxidation, α-oxycholestenol loses 2 atoms of hydrogen, and yields *oxycholestenone*, $C_{27}H_{40}O_2$; this is the chief product obtained on oxidising cholesterol in the manner mentioned above. It crystallises in large, colourless plates, and melts at 122—123°. It contains a carbonyl group, as it readily yields a *phenylhydrazone*, which crystallises in golden yellow, star-shaped crystals, melts at 271°, and gives a characteristic violet-red coloration when dissolved in concentrated sulphuric acid. It apparently contains no hydroxyl group, and does not give the typical cholestol reaction. On treatment with bromine in carbon bisulphide solution, it yields a *dibromo*-derivative, which melts at 167—168°, but it is uncertain whether this is an additive or a substitution product. The dibromo-derivative yields no hydrazone. Oxycholestenone, on further oxidation with an acetic acid solution of chromic anhydride, yields an acid whose *copper* salt has the composition $C_{27}H_{40}CuO_5$.

Oxycholestendiol, $C_{27}H_{42}O_3$, which is insoluble in cold benzene, crystallises from hot absolute alcohol in the form of minute, colourless prisms, melts at 231°, and is much more sparingly soluble than the compounds previously mentioned. It is insoluble in both cold and hot aqueous potash, does not give the characteristic cholestol reaction, and yields no phenylhydrazone. On treatment with alcoholic potash,

sulphuric acid, or hydrochloric acid, it is converted into oxycholestenone, and another substance which is being further investigated. Although it does not yield an acetyl-derivative, it seems probable that oxycholestendiol is an α-glycol.

Cholesterol, when more vigorously oxidised (with 24 atoms of oxygen instead of 6), yields a neutral substance, $C_{27}H_{40}O_5$, which melts at 171°, crystallises from alcohol, and does not yield a phenylhydrazone.

Cholesterylic acetate (1 mol.) is slowly oxidised when heated on the water bath with an acetic acid solution of chromic anhydride (6 atoms oxygen). Two compounds are thus formed which are best separated by 75 per cent. methylic alcohol.

β-oxycholestenol acetate, $C_{27}H_{41}O_2Ac$, which is only sparingly soluble in methylic alcohol, crystallises in four-cornered plates and melts at 152—153°. It does not combine with bromine, and does not form a phenylhydrazone. On hydrolysis with sodium methoxide, it yields *β-oxycholestenol*, which is isomeric with the α-compound described above; this crystallises in slender needles, melts at 157°, and does not combine with bromine. When the β-acetate is hydrolysed with alcoholic potash, the elements of water are also eliminated and *oxycholesterylen*, $C_{27}H_{40}O$, is obtained; this crystallises in colourless plates, melts at 112°, and yields a *dibromide* which decomposes at 91—92°. The other neutral product obtained on the oxidation of cholesterylic acetate crystallises from methylic alcohol (75 per cent.) in slender needles and is either $C_{29}H_{44}O_4$ or $C_{29}H_{46}O_4$. On hydrolysis, it yields a compound $C_{27}H_{42}O_3$ or $C_{27}H_{44}O_3$, which melts at 217—218°. Cholesterylic chloride, on oxidation, yields *oxychlorcholesten*, $C_{27}H_{41}ClO$, which crystallises in needles, melts at 121—122°, and does not combine with bromine.

The authors are at present investigating the acid products formed on the oxidation of cholesterol and its derivatives. J. J. S.

Flavone Derivatives, III. By PAUL FRIEDLÄNDER and R. LÖWY (*Ber.*, 1896, **29**, 2430—2435. Compare Abstr., 1896, i, 439).—In reply to the criticism of Kesselkaul and Kostanecki (Abstr., 1896, i, 606), the authors point out that the constitution of the compounds described by them as flavone derivatives rests on the same basis as that of chrysin, since the synthetical flavone derivatives, like this substance, yield acetophenone when heated with caustic soda.

The derivatives described below are obtained by acting with concentrated aqueous potash on a solution of chlorogallacetophenone and the aromatic aldehyde in water or dilute alcohol.

Dihydroxyflavone, prepared from benzaldehyde, has not yet been obtained pure. The *barium salt* crystallises in dark violet needles. The *dibenzoate* forms short, colourless needles, melting at 192·5—194°. The *monomethylic ether* crystallises in pale yellow needles, melts at 158°, and forms a yellowish-brown solution in aqueous soda. The neutral *dimethylic ether* also forms pale yellow needles, and melts at 148—149·5°. The *trihydroxyflavone* prepared from salicylaldehyde crystallises in yellow needles, melting at 214—216°. The *triacetate* forms white, silky needles, melting at 160°. The isomeric *compound* from metahydroxy-

benzaldehyde melts at 221—223°, and forms a *triacetate*, which melts at 166—167°. The *tribenzoate* melts at 173°. The third *isomeride*, from parahydroxybenzaldehyde, melts at 220°, and its *triacetate* at 199—201°. The *compound* obtained from metanitrobenzaldehyde crystallises well in reddish-yellow needles, and melts at 219—221°; the *acetate* melts at 218—219°. The *compound* formed from dimethylparamidobenzaldehyde crystallises in very sparingly soluble, lustrous, dark red tablets, melting at 203°, which dissolve both in acids and alkalis. The *acetate* forms silky, light red needles, and melts at 182°. Dichlorobenzaldehyde yields a *derivative* which crystallises in yellow needles, and melts and decomposes at 210°. The *acetate* is colourless, and melts and decomposes at 189—191°. The *condensation product* obtained from piperonal crystallises extremely well in reddish-yellow needles, which are very sparingly soluble in the usual solvents and melt at 221°; it forms a magenta-coloured solution in concentrated sulphuric acid. The *diacetate* forms needles which have a distinct yellow colour. The *dibenzoate* melts at 178°, and also forms yellow needles. The *compound* obtained from furfuraldehyde closely resembles the derivatives of the aromatic aldehydes; it crystallises in yellow needles, melting at 224—225°, and yields a *diacetate* which forms silky, pale yellow needles, melting at 201°. A. H.

Keto-Bromides from Asymmetrical Metaxylenol. By KARL AUWERS and E. ZIEGLER (*Ber.*, 1896, **29**, 2348—2355. Compare Abstr., 1896, i, 424).—An ethereal solution of tribromo-xylenol bromide (m. p. 135—136°), when reduced with zinc and hydrobromic acid, yields Jacobsen's tribromometaxylenol (Abstr., 1878, 410). The same compound when treated in acetone solution with water, yields 2 : 3 : 6-*tribromo-4-hydroxy-5-methylbenzylic alcohol*. This crystallises in glistening needles, melts at 174—176°, is readily soluble in alcohol, ether, acetone, chloroform, &c., but only sparingly in cold benzene and in light petroleum. It is also readily soluble in hot water containing bases in solution. On oxidation, it yields tribromotoluquinone (compare Canzoneri and Spica, Abstr., 1883, 330), and on treatment with methylic alcohol at 100° it is transformed into the methyl ether which has been previously described. This ether, when treated with hydrogen bromide in ice-cold methylic alcohol, is converted into tribromo-xylenol bromide (m. p. 134·5—136°).

"*Tribromo-xylenol acetate*," $CO<\begin{matrix}CMe:CBr\\CBr:CBr\end{matrix}>CMe\cdot OAc$, crystallises in flat, glistening needles, melts at 153—154°, and is soluble in most organic solvents, but insoluble in water and in alkalis. The *iodide*, obtained from the acetate by means of hydrogen iodide, melts at 134·5—135·5°.

Tribromo-xylenol bromide readily condenses with dimethylaniline to form the *additive compound* $OH\cdot C_6Br_3Me\cdot CH_2\cdot NMe_2PhBr$, which crystallises in white needles, and melts at 225—226° or 231—233°, according to the rapidity with which it is heated. It is converted, by the action of alkalis, into the *free base*, $OH\cdot C_6Br_3Me\cdot CH:NMe_2Ph$, which melts at 121—122°. Like the corresponding pseudocumene derivative, it readily unites with a molecule of methylic iodide; the

methiodide thus obtained melts at 154° and is decomposed by boiling water.

A condensation product, $OH \cdot C_6Br_3Me \cdot CH_2 \cdot C_9NH_7Br$, is obtained by the action of quinoline on tribromo-xylenol bromide. This melts at 232°, and is sparingly soluble in most organic solvents. It is readily soluble in alkalis, and is precipitated unaltered on the addition of an acid.

Piperidotribromo-xylenol, $OH \cdot C_6Br_3Me \cdot CH_2 \cdot C_5NH_{10}$, crystallises in small, glistening plates, melts at 155°, is readily soluble in most organic solvents, and is not altered by boiling with alkaline solutions. The pentabromo-derivative, tribromo-xylenol dibromide (Abstr., 1896, i, 424), when reduced with zinc and hydrobromic acid, yields the tribromo xylenol which melts at 179°, and when treated with sodium acetate and acetic acid, yields a *diacetate* which crystallises in flat needles, melts at 172—173°, and is readily soluble in most organic solvents. The diacetate, on treatment with hydrogen chloride in acetic acid solution, yields a *dichloride* which melts between 140° and 150°.

J. J. S.

Constitution of Dibromopseudocumenol Bromide and of its Derivatives. By KARL AUWERS and FRIEDR. BAUM (*Ber.*, 1896, **29**, 2329—2348. Compare Abstr., 1896, i, 149, 150, 420, 421, 423).—The dibromhydroxy-ψ-cumenol previously described (Abstr., 1896, i, 151) is shown to be a *dibromoparahydroxyparaxylobenzylic alcohol* [3 : 6-*dibromo-4-hydroxy-2 : 5-dimethylbenzylic alcohol*]. It is best prepared by the action of water on a boiling acetone solution of the dibromo-ψ-cumenol bromide. On treatment with acetic anhydride, it yields a monacetate which is insoluble in alkalis.

3 : 6-*Dibromo-4-methoxy-2 : 5-dimethylbenzylic alcohol* is obtained by treating the hydroxy-alcohol with sodium (1 mol.) and methylic iodide (slight excess) at 100° for 2—3 hours. It crystallises in slender needles, melts at 144°, is insoluble in alkalis, but readily soluble in most organic solvents. It reacts with phenylic cyanate at 100° to form the *urethane*, $OMe \cdot C_6H_2Me_2 \cdot CH_2 \cdot O \cdot CO \cdot NHPh$, which crystallises in long, colourless prisms, and melts at 157—158°.

The compounds previously described (Abstr., 1896, i, 150) as methoxy- and ethoxy-dibromopseudocumenol are really the alcoholic ethers of hydroxybenzylic alcohol. As such they readily react with methylic iodide and alkali to form 3 : 6-*dibromo-4-methoxy-2 : 5-dimethylbenzylic methylic ether*, $OMe \cdot C_6Br_2Me_2 \cdot CH_2 \cdot OMe$ (m. p. 102—103°), and the corresponding *ethoxy*-compound, $OEt \cdot C_6Br_2Me_2 \cdot CH_2 \cdot OMe$ (m. p. 98°). The latter is isomeric with 3 : 6-*dibromo-4-methoxy-2 : 5-dimethylbenzylic ethylic ether*, which melts at 39—40°. On boiling the hydroxy-alcohol with methylic or ethylic alcohol, it is gradually converted into its methyl (91—92°) or ethyl ether (85—87°). On passing hydrogen chloride into a methyl alcoholic solution of the hydroxy-alcohol, the only product formed is dibromo-ψ-cumenol chloride (m. p. 110—111°) (compare Abstr., 1896, i, 423), hydrogen bromide yields the corresponding bromide. The alcoholic ethers yield the same products when treated in a similar manner; the dimethylic

ether, however, is not acted on. No trace of ketonic chloride or bromide is obtained by passing hydrogen chloride or bromide into benzene solutions of the hydroxy-alcohol or of its ethers.

On treatment with dilute nitric acid (1 part of conc. acid to 3 parts of water), the hydroxy-alcohol is oxidised to Carstanjen's dibromoparaxyloquinone (Abstr., 1882, 612), and on reduction with sodium amalgam, in alkaline solution, yields a compound $C_9H_{12}O$ which melts at 183—184°.

The author has succeeded in synthesizing the hydroxy-alcohol from Fittig's 2 : 5 : 3-dibromonitroparaxylene (*Annalen*, 1868, **147**, 28; compare Jannasch, *Ber.*, 1877, **10**, 1356). A small quantity of the 3 : 6-*dinitro*-compound was also obtained on the nitration of dibromoparaxylene. It crystallises in colourless needles, and melts at 255°.

2:5:3-*Dibromamidoparaxylene* is obtained by reducing the mononitrocompound with iron and acetic acid. It is best purified by extracting the acid solution with ether, and then converting the base into its hydrochloride by passing hydrogen chloride into the ethereal solution. The hydrochloride is decomposed by boiling with water, and the base set free. It crystallises in small, colourless needles, melts at 91—92°, and is readily soluble in all organic solvents.

The corresponding 2 : 5-*dibromo*-1 : 4 : 3-*xylenol* is obtained in largest quantity on diazotising the amido-compound by Knoevenagel's method (Abstr., 1891, 54), and then adding the diazo-salt to a mixture of sulphuric acid and water heated at 110—120°, as recommended by Schmidt. Crystallised from light petroleum, it forms small needles, and melts at 90—91°. Its *benzoate* melts at 133·5°. It readily condenses with formaldehyde when treated according to the Lederer-Manasse method. The 3 : 6-dibromo-4-hydroxy-2 : 5-dimethylbenzylic alcohol thus obtained is identical with the hydroxydibromo-ψ-cumenol previously described.

The tribomo-derivative of ψ-cumenol when shaken with an aqueous solution of sodium sulphide yields the *sulphide*

$$(OH\cdot C_6Br_2Me_2\cdot CH_2)_2S.$$

It crystallises in long, colourless needles, melts at 243—245°, and is only sparingly soluble in most organic solvents. On oxidation with dilute nitric acid, it yields dibromoparaxyloquinone. When heated at 100° with methylic alcohol, methylic iodide, and alkali, it yields the *dimethoxy*-compound, $(OMe\cdot C_6Br_2Me_2\cdot CH_2)_2S$, which melts at 169°.

The dibromo-ψ-cumenol bromide, when treated with isobutyric acid and potassium isobutyrate yields an *isobutyrate*, which melts at 103—105°, and in most of its properties resembles the corresponding acetate.

The tribromo-ψ-cumenol bromide which is insoluble in alkalis (Abstr., 1896, i, 423) is shown to be $OH\cdot C{<}^{CBr\cdot CMe}_{CMe\cdot CBr}{>}C\cdot CH_2Br$. On oxidation, it yields the same dibromoparaxyloquinone as its isomeride which is soluble in alkalis. It moreover yields a *benzoate* which melts at 122°.

J. J. S.

Amidodiphenylic Sulphides. By RUDOLF NIETZKI and HEINRICH BOTHOF (*Ber.*, 1896, **29**, 2774—2775. Compare Abstr., 1895, i, 132).—The production of dinitrophenylic sulphide by the action of sodium sulphide on paranitrochlorobenzene in alcholic solution is not applicable to the meta-compound; sodium sulphide and metanitrochlorobenzene yield Laubenheimer's dichlor-azoxybenzene.

Orthodinitrophenylic sulphide is obtained from orthonitrochlorobenzene and sodium sulphide; it crystallises in golden, lustrous leaflets, and melts at 122—123°. *Orthodiamidophenylic sulphide* is formed on reducing the nitro-compound, and crystallises from hot water in colourless needles melting at 85—86°; the *diacetyl* derivative melts at 160°, and the *dibenzoyl* derivative at 162—163°. This thioaniline is not identical with Hofmann's paradiamidophenylic sulphide (Abstr., 1895, i, 87), although the two substances melt at the same temperature.

M. O. F.

Mercuriobenzylammonium Salts. By LEONE PESCI (*Gazzetta*, 1896, **26**, ii, 54—75).—*Mercuriobenzylammonium hydrate*,

$$HgNH(CH_2Ph)\cdot OH,$$

is obtained in solution by adding the calculated quantity of baryta water to a solution of the corresponding sulphate or by treating the corresponding chloride with silver oxide; it is a strong base and decomposes many salts of alkalis. The aqueous solution has an odour of benzylamine and an alkaline reaction, and absorbs carbonic anhydride from the air, depositing a white, amorphous powder. It reacts with sodium thiosulphate and potassium iodide in accordance with the equations $HgNH(CH_2Ph)\cdot OH + H_2O + Na_2S_2O_3 = HgS_2O_3 + 2NaOH + NH_2\cdot CH_2Ph$ and $HgNH(CH_2Ph)\cdot OH + H_2O + 2KI = HgI_2 + 2KHO + NH_2\cdot CH_2Ph$.

On adding benzylamine to aqueous mercuric chloride, a white *precipitate* is deposited having the composition

$$6HgNH(CH_2Ph)Cl,NH_2\cdot CH_2Ph,HCl;$$

when prepared in alcoholic solution, the precipitate contains only half the above proportion of mercuriobenzylammonium chloride. Mercuric chloride and benzylamine, in molecular proportion, react with formation of mercuriobenzylammonium chloride and benzylamine hydrochloride, and the latter is in part tenaciously held by the former. The double salt, $6HgNH(CH_2Ph)Cl,NH_2\cdot CH_2Ph,HCl$, when treated with very dilute potash, yields benzylamine and *mercuriobenzylammonium chloride*; the latter is a white, amorphous powder insoluble in the ordinary solvents, and is decomposed by potassium iodide, ammonium bromide and sodium thiosulphate solutions in accordance with the equations $HgNH(CH_2PH)Cl + 2KI + H_2O = HgI_2 + KCl + KHO + NH_2\cdot CH_2Ph$ and $HgNH(CH_2Ph)Cl + 2NH_4Br = HgBr_2 + 2NH_3 + NH_2\cdot CH_2Ph$ and $HgNH(CH_2Ph)Cl + Na_2S_2O_3 + H_2O = HgS_2O_3 + NaCl + NaOH + NH_2\cdot CH_2Ph$. The compound prepared by André (Abstr., 1891, 1030) by treating mercuric chloride with benzylamine was identical with this chloride.

A double *compound* of the composition

$$HgNH(CH_2Ph)Cl,NH_2\cdot CH_2Ph,HCl,HgCl_2,$$

is prepared by boiling the precipitate obtained from mercuric chloride and benzylamine with mercuric chloride solution; it crystallises in colourless, pearly laminæ insoluble in the ordinary solvents, and is decomposed by hydrogen sulphide with formation of hydrogen chloride, mercuric sulphide and benzylamine hydrochloride. It is decomposed by potassium iodide, ammonium bromide, and sodium thiosulphate, in the same way as the other salts of the base.

Mercuriobenzylammonium sulphate, $(HgNH\cdot CH_2Ph)_2SO_4$, is precipitated on adding the calculated quantity of sodium sulphate to a solution of the double acetate described below; it is a white, amorphous powder, insoluble in the ordinary solvents. A double *salt* of the composition $(HgNH\cdot CH_2Ph)_2SO_4,(NH_2\cdot CH_2Ph)_2,H_2SO_4$, is deposited on adding benzylamine to sulphuric acid; it is a white powder, and is not separated into its constituents by water.

A double *nitrate* of the composition

$$HgNH(CH_2Ph)NO_3,NH_2\cdot CH_2Ph,HNO_3,$$

is prepared by boiling the precipitate obtained by adding benzylamine to a slightly acid solution of mercuric nitrate with its mother liquor; on cooling, the salt separates in colourless, brilliant laminæ. Mercuriobenzylammonium nitrate could not be prepared.

A double *acetate* of the composition

$$HgNH(CH_2Ph)\cdot C_2H_3O_2,NH_2\cdot CH_2Ph,C_2H_4O_2,$$

is deposited in lustrous rectangular plates on adding benzylamine to a saturated aqueous solution of mercuric acetate; it may be crystallised from hot water, in which it is very soluble. Mercuriobenzylammonium acetate could not be prepared. W. J. P.

Enantiomorphic Phenethylamines. By JOHAN M. LOVÉN (*Ber.*, 1896, **29**, 2313—2318).—Phenethylamine, $NH_2\cdot CHMePh$, prepared from acetophenoxime by reduction, yields two distinct compounds on conversion into the hydrogen tartrate. From the concentrated solution of the salt, slender needles containing $1\frac{1}{2}H_2O$ first separate; these, on reconversion into the base, yield a slightly dextro-rotatory compound (+0·75°). From the mother liquor of the needles, anhydrous prismatic crystals separate after a time, and these on treatment with potash yield a base which is strongly lævo-rotatory (−8·5° in a 200 mm. tube).

The figures given for the rotatory powers do not pretend to any great accuracy, it being merely intended to show the possibility of resolving inactive phenethylamine into its optical components. J. F. T.

Behaviour of Orthonitroparaphenylenediamine towards Nitrous Acid. By CARL BÜLOW (*Ber.*, 1896, **29**, 2284—2287).—It has been observed by Ladenburg that the action of nitrous acid on orthonitroparaphenylenediamine gives rise to a brown, amorphous powder, but the exact nature of the substance has not been investigated. On adding a 20 per cent. solution of sodium nitrite to a solution of orthonitrophenylenediamine hydrochloride in acetic acid, the author has obtained *metanitroparamidodiazobenzene*, along with a very small quantity of the amorphous, brown substance, which is probably a tetrazo-compound. When the diazo-compound is treated

with sodium β-naphthol-3 : 6-disulphonate, lustrous, green needles rapidly separate, appearing dark blue by transmitted light.

On adding sodium nitrite to an acid solution of paramidometanitrodiazobenzene, the amido-group is diazotised, the diazonitro-azo-compound separating as a bluish-red precipitate.

Paramidometanitrodiazobenzene and sodium paramidometanitrobenzeneazo-β-naphtholdisulphonate are converted into the corresponding nitrosamines by caustic alkali, these substances being indifferent towards sodium 2-naphthol-3 : 6-disulphonate. Mineral acids, on the other hand, convert them into the diazo-compounds. M. O. F.

Action of Sodium on Aromatic Nitriles. By C. A. Alfred Lottermoser (*J. pr. Chem.*, 1896, [2], **54**, 113—143).—Walther has shown (Abstr., 1894, i, 503) that when benzonitrile (2 mols.), aniline (1 mol.) and sodium (2 atoms) are heated together in benzene, phenylbenzenylamidine is obtained. The contents of the flask are poured into alcohol to dissolve remaining sodium, and the whole is then diluted with water, acidified with acetic acid, and heated on the water bath until hydrogen cyanide and benzene have been eliminated. By further dilution, some impurities are separated; these are filtered off and ammonia is added to the filtrate, which is then stirred until the new base is precipitated. The yield is about 84 per cent. of that calculated from the equation $2PhCN + PhNH_2 + Na_2 = C_6H_6 + NaCN +$ NHPh·CPh:NNa. The position of the sodium in the sodium derivative which is first produced has not been determined with certainty. *Diacetophenylbenzenylamidine*, NPhAc·CPh:NAc, is crystalline and melts at 128—130°; it is produced by heating the amidine with acetic anhydride, a treatment which generally fails to replace both atoms of hydrogen in an amido-group by acetyl, so that the amidine must have the constitution corresponding with the above formula rather than that represented by NH_2·CPh:NPh.

By heating phenylbenzenylamidine with phenylhydrazine hydrochloride, or phenylbenzenylamidine hydrochloride with phenylhydrazine, the *phenylhydrazide*, NHPh·CPh:N·NPh is formed; it melts at 174°, and is apparently identical with von Pechmann's anilamidobenzenylphenylimidine (Abstr., 1896, i, 32), to which, however, the formula NPh:CPh·NH·NHPh has been assigned, chiefly because of the power that the compound has of reducing mercuric oxide. The *oxime*, NHPh·CPh:NOH, is formed in white needles when hydroxylamine hydrochloride and the amidine are warmed together and ammonia is added by degrees; it melts at 135—136°.

Orthotolylbenzenylamidine, prepared like the phenylamidine, crystallises in small needles, melts at 105—108°, and dissolves freely in alcohol, ether, and chloroform, less freely in benzene, and very sparingly in light petroleum. Paratolylbenzenylamidine, already described by Bernthsen, is only produced from paratoluidine if ether be substituted for benzene in the prescription for the phenylamidine. When benzene is the solvent, a *compound*, $C_{17}H_{14}N_2$, is produced, which crystallises in lustrous, yellow laminæ, melts at 121—123°, and dissolves easily in ether and chloroform, but only sparingly in alcohol; the *platinochloride* was prepared. To ascertain whether the para-position of the methyl

to the amido-group is the conditioning factor in the abnormal behaviour of paratoluidine, metaxylidine was submitted to the reaction. *Metaxylylbenzenylamidine* was, however, obtained; it crystallises in colourless needles, and melts at 106—107°.

Phenylacetophenylamidine, $CH_2Ph\cdot C(NHPh):NH$, was prepared by the action of sodium on aniline and benzylic cyanide in benzene; it is identical with Bernthsen's compound obtained from benzylic cyanide and aniline hydrochloride (Abstr., 1876, ii, 95); it melts at 139°.

Phenylorthotolenylamidine, prepared from aniline and orthotoluonitrile by the action of sodium, ether being used instead of benzene, melts at 121—123°, and shows nearly the same solubility as the foregoing amidines. *Phenylparatolenylamidine,* similarly prepared, melts at 149°; its *diacetyl*-derivative melts at 121—122°.

Phenyl-β-naphthenylamidine, from aniline and β-naphthonitrile, crystallises in small, lustrous laminæ, and melts at 162—163°. *Phenyl-α-naphthenylamidine* melts at 128—130°.

It is noticeable that the amidines made from benzonitrile, tolunitrile, and naphthonitrile decrease in solubility in alcohol, benzene, ether, chloroform, and light petroleum in the order in which they have been named. This is also the case with the yield of amidine obtainable.

A compound, $C_{27}H_{21}N_3$, believed to be *tetraphenyldihydrotriazine,* $NH<\begin{matrix}CPh:N\\CPh_2\cdot N\end{matrix}>CPh$, is obtained by heating benzonitrile (2 mols.) with sodium (1 atom) in benzene for several days on the water bath; light petroleum is added, and the precipitate is dried on a clay-plate and added cautiously to water, whereby the sodium cyanide is removed from the insoluble new compound, which is finally crystallised from alcohol. Some cyaphenine is also formed in the reaction. The triazine crystallises in long, white needles, melts at 190—191°, and dissolves sparingly in alcohol, but more freely in benzene, ether, and chloroform. The *hydrogen chromate,* $C_{27}H_{21}N_3,H_2CrO_4$, the *hydrochloride,* $C_{27}H_{21}N_3,HCl$, the *hydrogen sulphate,* and the *platinochloride* (with $1H_2O$) are described. When heated with alcoholic potash, the base yields potassium benzoate, ammonia, and benzophenone; when heated with phenylhydrazine hydrochloride in alcohol, it yields benzophenone hydrazone, ammonium chloride, and benzonitrile. These facts are considered indicative of the constitution ascribed to the compound.

A. G. B.

Phenylhydroxylamine. By CARL GOLDSCHMIDT (*Ber.*, 1896, **29**, 2307).—Phenylhydroxylamine is most advantageously prepared by dissolving nitrobenzene in 10 parts of ether containing a few c.c. of water, and heating with excess of zinc dust and some calcium chloride for 3 hours on the water bath. This modification of the method of Wohl and Bamberger gives rise to a product which is free from aniline. M. O. F.

Nitrosophenylhydroxylamine. By EUGEN BAMBERGER and THOR EKECRANTZ (*Ber.*, 1896, **29**, 2412—2414).—The method of obtaining methylic derivatives by means of diazomethane, due to von Pechmann (Abstr., 1895, i, 328, 493), has been applied by the authors to nitrosophenylhydroxylamine.

Nitrosophenylhydroxylamine methyl ether, $O<\begin{matrix}NPh\\ |\\ N\cdot OMe\end{matrix}$, dissolves readily in cold organic solvents excepting light petroleum, and crystallises in colourless prisms melting at 37—38°; it is obviously isomeric with the α- and β-methylic salts of benzenediazoic acid (Abstr., 1894, i, 238), but is distinguished from these compounds by its greater stability, being volatile without decomposition in an atmosphere of steam, and developing no coloration with naphthylamine acetate. M. O. F.

Action of Hydroxylamine on Nitro-compounds. By OTTO W. SCHULTZE (*Ber.*, 1896, **29**, 2287—2290. Compare Abstr., 1896, i, 613).—*Dinitronitrosophenylhydroxylamine*, $C_6H_3(NO_2)_2\cdot N_2O_2H$, is obtained on adding a solution of hydroxylamine hydrochloride, neutralised with sodium carbonate, to symmetrical trinitrobenzene in presence of caustic potash, and cautiously acidifying the cooled solution with hydrochloric acid; it separates from ethylic acetate in prismatic crystals having a bluish-red reflex, and melts at 184—185°. Hydroxylamine is without action on ortho- or meta-dinitrobenzene.

When nitromethane is dissolved in caustic potash and allowed to remain with excess of hydroxylamine hydrochloride, Lecco's methazonic acid (this Journal, 1876, ii, 287) is formed; the *potassium* derivative crystallises in beautiful, white needles, and explodes when heated, a bright blue flame being produced.

Ethazonic acid, obtained from nitroethane and hydroxylamine, is a substance which crystallises very readily, and melts at 93°, with rapid disengagement of nitric peroxide. M. O. F.

Constitution of Hydroxyazo-compounds. By KARL AUWERS (*Ber.*, 1896, **29**, 2361—2362. Compare Goldschmidt, Abstr., 1891, 1209, and 1892, 974; McPherson, Abstr., 1896, i, 27).—According to Goldschmidt, the hydroxyazo-compounds are all to be regarded as quinone hydrazones, whereas McPherson regards the para-compounds as true hydroxy-derivatives and the ortho-compounds as hydrazones. The author has undertaken an examination of some 20 hydroxyazo-compounds as regards their cryoscopic behaviour in naphthalene solution. The results agree with those drawn by McPherson from chemical considerations.

The para-compounds gave abnormal results, thus indicating their hydroxylic nature (compare Abstr., 1894, ii, 133; 1895, ii, 41; and 1896, ii, 293). The ortho-compounds gave quite normal results, as did also certain undoubted hydrazones which the author investigated.

These remarks apply only to the free hydroxyazo-compounds and not to their salts or ethers. J. J. S.

Oxidation of Phenylbenzylidenehydrazone. By GAETANO MINUNNI and E. RAP (*Gazzetta*, 1896, **26**, i, 441—456).—On oxidising phenylbenzylidenehydrazone with yellow mercuric oxide in a 4·5 per cent. chloroform solution on the water bath, dehydrophenylbenzylidenehydrazone and a little diphenyldibenzylidenehydrotetrazone are obtained; the former alone is produced if the oxidation is carried out in an ethereal or a 2 per cent. chloroform solution. Phenylbenzylidenehydrazone is readily oxidised by boiling with amylic nitrite

in ethereal solution; in this case, dehydrophenylbenzylidenehydrazone is produced in much greater quantity than the tetrazone.

Diphenyldibenzylidenehydrotetrazone melts at 180—181° in a previously heated bath, but if heated slowly, it is converted into dehydrophenylbenzylidenehydrazone and then melts at 185—190°; the misunderstanding between Minunni (Abstr., 1893, i, 97), von Pechmann (Abstr., 1893, i, 461), and Ingle and Mann (Trans., 1895, 606), arises from this fact. The tetrazone crystallises in thin, yellow needles, and is sparingly soluble in the usual solvents. Dehydrophenylbenzylidenehydrazone crystallises in thin, colourless needles which melt at 198—200° when slowly heated, but at 205° if rapidly heated; it is readily obtained by heating the tetrazone at 180°. In the oxidation with amylic nitrite, these two products are accompanied by small quantities of an oxygenated *compound* crystallising in needles which do not melt at 240°.

On heating diphenyldibenzylidenehydrotetrazone with benzoic chloride on a salt water bath, a *substance*, $C_{14}H_{10}N$, is obtained which crystallises in pearly, white laminæ melting at 211·5—212·5°; on heating the tetrazone with benzoic or acetic chloride on a water bath, the principal product is a crystalline *compound* melting at 178—179°. The substance melting at 211·5—212·5° is also obtained by heating β-benzilosazone with benzoic chloride on a salt water bath.

On heating dehydrophenylbenzylidenehydrazone with benzoic chloride at 100°, a small proportion of the substance melting at 211·5—212·5° is obtained; at lower temperatures a crystalline *compound* melting at 173° and a *monobenzoyl*-derivative, $C_{26}H_{21}N_4\cdot COPh$, of dehydrophenylbenzylidenehydrazone, which crystallises in lustrous, white needles melting at 186—188° are produced. The substance melting at 173° can be converted into the benzoyl derivative by heating it above its melting point. W. J. P.

The Methyl-, Ethyl-, Amyl- Allyl-, and Benzyl-phenylhydrazones, and the β-naphthylhydrazones of the Sugars. By W. Alberda Van Eckenstein and Cornelis A. Lobry de Bruyn. (*Rec. Trav. Chim.*, 1896, **15**, 225—229).—The authors have pointed out (Abstr., 1896, i, 588) that the above hydrazones might be of considerable service in the identification and separation of certain sugars. In the present communication, a list is given in tabular form of the alkylated phenylhydrazones and β-naphthylhydrazones of galactose, mannose, arabinose, rhamnose, glucose, xylose, lactose, maltose, and melibiose, together with their melting points, specific rotatory powers in methylic alcohol and glacial acetic acid solutions, and statements as to their colour and solubility in water and methylic and ethylic alcohols. These compounds were prepared by adding to a hot concentrated solution of the sugar the equivalent quantity of the hydrazine dissolved in the molecular proportion of glacial acetic acid. When boiled with benzaldehyde in aqueous solution, they all undergo quantitative decomposition and may consequently be utilised for the preparation of certain of the sugars in a state of purity. No alkylphenylhydrazones were obtained in the case of fructose, sorbose, maltose and xylose, and of these four, maltose and xylose alone yielded β-naphthyl-

hydrazones. The methyl- and ethyl-phenylhydrazones of glucose and lactose could not be prepared. The benzyl-, allyl- and amyl-hydrazones of galactose have the property of forming jellies when their boiling solutions (0·1—0·25 gram in 25 c.c. water) are rapidly cooled.

A. C. C.

Isomeric Nitrosodiethylphloroglucinols. By D. MOLDAUER (*Monatsh.*, 1896, **17**, 462—478).—A strong solution of diethylphloroglucinol (1 mol.) in caustic potash containing potassium nitrite (2 mols.) is mixed at 0° with acetic acid; the whole, after being allowed to remain during 2—3 hours at the ordinary temperature, is filtered, the insoluble portion washed with ice-cold water to eliminate all inorganic salts, and dried at 50—60°; it is then extracted with absolute ether in which one portion is soluble and the other, which is insoluble, is obtained in the form of slender, light yellow needles.

The ethereal solution, on evaporation, deposits *a-diethoxyquinonoxime*, $C_{10}H_{13}NO_4$, which forms dark red leaflets, melts at 117° (uncorr.), and sublimes at higher temperatures suffering slight decomposition; it dissolves in most media, and with dilute alkalis forms a dark brown solution from which it is precipitated on acidification; it gives Liebermann's nitroso-reaction. The *potassium* salt, $C_{10}H_{12}NO_4K$, crystallises in beautiful, grass-green needles and is soluble in alcohol; the *silver* salt forms minute, reddish-brown crystals insoluble in water.

The insoluble substance *β-diethoxyquinonoxime* crystallises from alcohol or boiling water in small, woolly needles, melts and decomposes at 192—195°, dissolves in alkali forming a reddish-brown solution, and gives Liebermann's reaction. The *potassium* salt, $C_{10}H_{12}NO_4K + H_2O$, forms small, blue-violet crystals, and is excessively soluble in water; the *silver* salt is obtained as a green, microcrystalline precipitate.

The potassium salt of α-diethoxyquinonoxime reacts with ethylic iodide at the temperature of the water bath and the product consists of two salts, which may be separated by fractional precipitation from alcohol. The more soluble portion, *α-diethoxyquinonoxime ethylic ether*, $C_6H_2NO(OEt)_3$, crystallises in small, red, prismatic crystals, melting at 106°; it is slowly dissolved and decomposed by hot water or dilute alkali.

The more sparingly soluble substance crystallises in colourless, shining triclinic tables, melts at 60°, is insoluble in water, but dissolves readily in ether, benzene, and petroleum; it does not give Liebermann's reaction. It has the molecular formula $C_{12}H_{15}NO_3$, and appears to be formed directly from the oxime, as it cannot be obtained from the foregoing substance; it contains, moreover, only two ethoxyl groups. Several provisional constitutions are suggested for it, but for the present the authors prefer to use the name *ethylpyriphlorone diethylic ether*. The following salts have been prepared from it; the *hydrochloride*,

$$C_{12}H_{15}NO_3,HCl,$$

crystallises in long, silky needles, and melts, evolving hydrogen chloride, at 72—78°, and is readily decomposed; the *platinochloride*,

$$(C_{12}H_{15}NO_3)_2,H_2PtCl_6,$$

crystallises from a mixture of alcohol and hydrochloric acid in slender needles.

Ethylic iodide also acts on β-diethoxyquinonoxime; the product consists of a *triethylic* ether, $C_6H_2NO(OEt)_3$, which dissolves readily in nearly all the ordinary media, crystallises in yellow, silky needles, melts at 117—118°, and distils unaltered at higher temperatures, the vapours solidifying to large, colourless needles.

α-Diethoxyquinonoxime is reduced by stannous chloride and hydrochloric acid, an ethyl group being simultaneously removed; the *product* $C_8H_{11}NO_3,HCl$ forms an unstable, white, crystalline mass. The oxime also reacts with phenylhydrazine and with hydroxylamine, yielding, in the former instance, a *substance* which turns brown below 152°.

A. L.

Conversion of α-Aldoximes into Nitriles. By GAETANO MINUNNI and D. VASSALLO (*Gazzetta*, 1896, **26**, i, 456—465).—On treatment with ether saturated with hydrogen chloride at −10°, the benzoyl derivatives of α-metanitrobenzaldoxime, α-cuminaldoxime, α-anisaldoxime, α-salicylaldoxime, α-furfuraldoxime and α-propaldoxime are converted into the corresponding nitriles and acids, just as benzoyl- or acetyl-α-benzaldoxime is converted into benzonitrile and benzoic acid (Minunni, Abstr., 1893, i, 89); the reaction is represented by the equation R·CH:NO·CO·R = R·C:N + R·COOH.

Both α- and β-oximes can therefore be directly converted into the corresponding nitriles at ordinary temperatures, the former by the action of ethereal hydrogen chloride, and the latter by treatment with alkali carbonates; the α-oximes do not previously change into their β-isomerides, for ethereal hydrogen chloride converts β-benzoylbenzaldoxime into the α-modification.

Benzoyl-α-cuminaldoxime, $C_6H_4Pr·CH:NO·COPh$, crystallises in long, white needles melting at 125—126°; *cuminonitrile*, $C_6H_4Pr·CN$, is an oil boiling at 239—241°. *Anisonitrile* crystallises in long, white needles melting at 59—60°.

Benzoyl-α-furfuraldoxime, $C_4OH_3·CH:NO·COPh$, crystallises in broad, white laminæ melting at 138—138·5°.

W. J. P.

Benzylation of Acetaldoxime. By ALFRED WERNER (*Ber.*, 1896, **29**, 2667).—The bye-product obtained by the author and H. Buss in benzylating acetaldoxime, and supposed by them to be a nitrogen ether (Abstr., 1896, i, 461), is found to be identical with the dibenzylhydroxylamine described by Beckmann and A. Köster (Abstr., 1893, i., 464).

A. L.

The "Beckmann Rearrangement." I. Chlorimido-ethers. By JULIUS STIEGLITZ (*Amer. Chem. J.*, 1896, **18**, 751—761).—The author has made experiments in order to determine to what extent, if at all, the remaining hydrogen atom in the group −CO·NHBr is necessary for the molecular rearrangement of the acid bromamides which occurs when these substances are heated with aqueous alkali. He suggests that the alkali causes a direct loss of hydrogen bromide, producing the

group (RCO)N: with a univalent nitrogen atom whose reactivity would be the cause of the separation of the alkyl from the carbon atom in union with the nitrogen, thus producing isocyanates. It is remarked that this assumption makes it possible to satisfactorily explain several important reactions, such as the exchange which occurs when oximes are treated with phosphorus pentachloride (Beckmann rearrangement), and the production of isocyanates from the acid azides on warming them with water or alcohol.

Benzochlorimidoethyl ether (chlorimidoethyl benzoate), OEt·CPh:NCl, was prepared by the action of a mixture of sodium hypochlorite and hypochlorous acid on the hydrochloride of benzimidoethyl ether. It is a colourless, mobile oil, which boils at 130—132° (16 mm.) and is readily soluble in the usual organic solvents, insoluble in water, aqueous acids, and alkalis. Attempts to convert this compound into two stereoisomerides were unsuccessful. In alcoholic solution aqueous ammonia at once causes an evolution of nitrogen; hydrochloric acid an evolution of chlorine. When benzochlorimidoethyl ether was slowly heated, a vigorous reaction occurred, resulting in the formation of benzonitrile (and decomposition products of ethylic hypochlorite) together with smaller quantities of benzamide and of an aniline derivative which was not identified.

The direct exchange, therefore, of the phenyl group and the chlorine atom (forming ethyl phenylimidochlorformate), if it takes place at all, must occur to a very slight extent. It is possible that such a rearrangement might occur more readily in the case of the stereoisomeride of the compound (? "anti-") used by the author, if it could be prepared.

Benzobromimidoethyl ether was prepared by the action of sodium hypobromite on the benzimidoethyl ether hydrochloride. It is a yellowish oil, gradually decomposed by water, and at once by hydrochloric acid or concentrated aqueous ammonia. When heated, it behaves like the chlorimide, giving benzonitrile as the chief product. These results confirm those obtained by Slosson (Abstr., 1896, i, 216) with the acid chloranilides, and appear to show that the hydrogen atom in the group –CO·NHBr is necessary for the "Beckmann rearrangement." They are also in perfect accord with the interpretation of the reaction given above. A. C. C.

Diacid Anilides. By Henry L. Wheeler (*Amer. Chem. J.*, 1896, **18**, 695—702. Compare Abstr. 1896, i, 478, 609).—The anilides described in this paper were prepared by suspending silver formanilide or mercury acetanilide in dry ether or benzene, and adding the appropriate proportion of acid chloride; the action was generally complete in a few minutes, and on filtering off the silver chloride or mercuric chloride and evaporating the filtrate the anilide was isolated. These anilides react with alkalis with separation of the lower acid radicle, and formation of the anilide of the higher acid.

Formacetanilide, NPhAc·CHO, forms colourless, prismatic crystals, melts at 56°, and dissolves in alcohol, ether, benzene, and sparingly in light petroleum.

Formopropionanilide, CHO·NPh·COEt, is an oil which does not

solidify in a freezing mixture, and decomposes when heated at 18 mm. yielding propionanilide.

Formobutyranilide, $COPr^{a}\cdot NPh\cdot COH$, is also an oil which cannot be solidified or distilled unchanged.

Formostearanilide, $C_{17}H_{35}\cdot CO\cdot NPh\cdot COH$, forms colourless crystals, melts at 61°, and is very soluble in benzene, chloroform, light petroleum, carbon bisulphide, and ether, but less soluble in cold alcohol.

Acetopropionanilide, $NPhAc\cdot COEt$, is a clear, colourless oil which boils at 159—160° (? 18 mm.), and does not solidify; it dissolves readily in ether and benzene.

Acetobutyranilide, $COPr^{a}\cdot NPhAc$, is a clear, colourless oil, boiling at 163° (18 mm.).

Acetisovaleranilide, $C_4H_9\cdot CO\cdot NPhAc\cdot$, is an oil which boils at 164—165° (18 mm.).

Acetopalmitanilide, $C_{15}H_{31}\cdot CO\cdot NPhAc$, forms colourless, microscopic crystals, and melts at 60—61°.

The action of silver and mercury benzamide on acid chlorides does not yield diacid amides, as might be expected by analogy with the foregoing results; instead, benzonitrile is the chief product.

A. G. B.

Action of Ethylic Oxalate on Aromatic Amido-compounds.

By RICHARD E. MEYER and ALB. SEELIGER (*Ber.*, 1896, **29**, 2640—2645).—*Orthophenyleneoxamide*, $C_6H_4<\begin{matrix}NH—CO\\ |\\ NH—CO\end{matrix}$, is formed when orthophenylenediamine is treated with ethylic oxalate. It forms long, lustrous needles, decomposes at high temperatures without melting, is very sparingly soluble in ether, acetone, benzene and xylene, but dissolves to a considerable extent in petroleum and methylic and ethylic alcohols, separating from these solutions in beautiful crystals. It dissolves readily in dilute aqueous alkalis, and is reprecipitated by carbonic anhydride.

Orthotolyleneoxamide, $C_6H_3Me<\begin{matrix}NH—CO\\ |\\ NH—CO\end{matrix}$, prepared from orthotolylenediamine $[Me:(NH_2)_2 = 1:3:4]$, crystallises in needles, decomposes without melting when heated, is scarcely soluble in ether, acetone or benzene, but is appreciably dissolved by chloroform, ethylic acetate, light petroleum and xylene, and is soluble in boiling water, methylic and amylic alcohols. Its behaviour towards alkalis resembles that of orthophenyleneoxamide.

Ethylic metaphenylenedioxamate, $C_6H_4(NH\cdot CO\cdot COOEt)_2$, is produced when metaphenylenediamine reacts with ethylic oxalate. It crystallises in small needles, melts at 154°, and dissolves readily in most of the usual media; it is quickly hydrolysed by dilute aqueous alkalis, with production of free *metaphenylenedioxamic acid*, $C_6H_4(NH\cdot CO\cdot COOH)_2$, which crystallises from methylic, ethylic, and amylic alcohols, but is very sparingly soluble in ether, acetone, chloroform, benzene, xylene, and light petroleum; when heated, it sinters, melting finally at 225—230°.

Metaphenylenedioxamide, $C_6H_4(NH\cdot CO\cdot CONH_2)_2$, prepared by treat-

ing the foregoing ethylic salt with aqueous ammonia, forms microscopic needles, melting at 290°, is insoluble in the ordinary media, and is hydrolysed by hot soda or strong acids.

Ethylic paraphenylenedioxamate, $C_{14}H_{16}N_2O_6$, resembles the corresponding meta-compound in most particulars, and melts at 215°.

Paraphenylenedioxamide, $C_{10}H_{10}N_4O_4$, froms a crystalline powder and does not melt at 310°.

Orthodihydroxydiphenyloxamide, $C_2O_2(NH{\cdot}C_6H_4{\cdot}OH)_2$, is the product of interaction of orthamidophenol and diethylic oxalate; it crystallises from hot alcohol in yellowish-brown leaflets, melts at 280—282° and is somewhat soluble in methylic, ethylic, and amylic alcohols, but is only sparingly dissolved by benzene and xylene, whilst it appears to be nearly insoluble in light petroleum, ether, and ethylic acetate; it dissolves in alkalis and in hot dilute acids, forming yellow and red solutio s respectively. The *diacetyl* compound, $C_2O_2(NH{\cdot}C_6H_4{\cdot}OAc)_2$, melts at 201°.
A. L.

Action of Ammonia and Alkylamines on Bromethylphthalimide.

By EUGEN RISTENPART (*Ber.*, 1896, **29**, 2526—2533).—When bromethylphthalimide and diethylamine are heated at 100°, *diethylamidoethylphthalimide* [Phthalyldiethylethylenediamine],

$$C_8H_4O_2{:}N{\cdot}C_2H_4{\cdot}NEt_2,$$

is produced, but has not been isolated on account of its ready solubility; hydrolysis with 20 per cent. hydrochloric acid resolves it into phthalic acid, and *as-diethylethylenediamine*, $NH_2{\cdot}C_2H_4{\cdot}NEt_2$, a mobile, alkaline liquid, which boils at 145°, and has the sp. gr. = 0·827 at 18·5°/18·5°. The *platinochloride* melts at 230°, and the *aurochloride* at 161—163°; the *picrate* melts at 211°, the carbon bisulphide *compound* at 159°, and the *thiocarbamide* at 86°. The action of diethylamine on bromethylphthalimide also gives rise to hydroxyethylphthalimide (Abstr., 1888, 440).

Phthalo-β-bromodiethylamide, $NHEt{\cdot}CO{\cdot}C_6H_4{\cdot}CO{\cdot}NH{\cdot}C_2H_4Br$, is obtained from bromethylphthalimide and ethylamine in alcoholic solution at 0°, and melts at 127°; at higher temperatures *phthalo-ethylvinylamide*, $NHEt{\cdot}CO{\cdot}C_6H_4{\cdot}CO{\cdot}NH{\cdot}C_2H_3$, is produced, and when crystallised from petroleum melts at 106—107°. As in the previous case, hydroxyethylphthalimide is also formed. The *platinochloride* of phthalo-ethylvinylamide melts at 195—196°; the *aurochloride* melts at 125—127°, and the *picrate* at 172°.

Methylamine converts phthalobromethylimide into phthalomethylimide, and ammonia gives rise to β-hydroxyethylphthalimide; along with this substance is formed *triphthalyltriimidotriethylamine*,

$$N(C_2H_4{\cdot}N{<}{}^{CO}_{CO}{>}C_6H_4)_3,$$

which crystallises from glacial acetic acid, and melts at 187·5°. The *hydrobromide* melts at 235°, and the *hydrochloride* at 244·5°. *Triamidotriethylamine*, $N(C_2H_4{\cdot}NH_2)_3$, is obtained by hydrolysing the phthalyl derivative with concentrated hydrochloric acid, and forms a viscous liquid which boils at 263°, under a pressure of 744 mm., and has the sp. gr. = 0·977 at 19°/19°; the *hydrochloride* and *hydrobromide* do not

melt below 300°, and the *platinochloride*, which blackens at 250°, melts and effervesces at 280°. The *aurochloride* melts and decomposes at 185°, and the *picrate*, which contains $2H_2O$ at 225°; the *tribenzoyl* derivative crystallises in six-sided plates, and melts at 148—149°. M. O. F.

Derivatives of Amidoguanidine. By GUIDO PELLIZZARI (*Gazzetta*, 1896, **26**, ii, 174—193. Compare Pellizzari and Cuneo, Abstr., 1894, i, 516).—*Benzylideneamidophenylguanidine*, $NH_2\cdot C(NH)\cdot NPh\cdot N\colon CHPh$, is obtained by treating the aqueous solution of the syrupy amidophenylguanidine (Abstr., 1892, 579) with benzaldehyde; benzylidenephenylhydrazine separates, and on adding an alkali nitrate, *benzylideneamidophenylguanidine nitrate*, $C_{14}H_{14}N_4,HNO_3$, is deposited; it crystallises in long, colourless needles melting and decomposing at 219°. The *picrate* crystallises in yellow needles melting at 242°, whilst the *platinochloride* crystallises in small needles melting at 215°, and is partially reduced on boiling in alcoholic solution. The free base is obtained by treating the nitrate with potash and extracting with ether; it separates in large crystals melting at 133°, and is very soluble in alcohol, benzene, or ether, but only sparingly so in water. It readily changes to an uncrystallisable oil on boiling with benzene, and when treated with potash is converted into benzylidenephenylhydrazine. On boiling an aqueous solution of the nitrate for many hours, benzaldehyde is slowly given off, and pure salts of *amidophenylguanidine*, $NH_2\cdot C(NH)NPh\cdot NH_2$, can be obtained from the solution. The base is prepared by treating the nitrate with potash; it is an oil which slowly crystallises, and is very soluble in alcohol or ether. It reduces Fehling's solution or ammoniacal silver nitrate, and absorbs carbonic anhydride from the air. The *nitrate*, $C_7H_{10}N_4,HNO_3$, crystallises in hard, colourless, monosymmetric prisms, melting at 143°, and is very soluble in water;

$$a : b : c = 0.5065 : 1 : 0.2567.\ \beta = 85°47'.$$

The *picrate* crystallises in yellow needles melting at 179°, and is sparingly soluble in water; the *platinochloride* forms small, yellow crystals, and is soluble in alcohol or water. A double *salt* of the composition, $(C_7H_9N_4)_2Cu,2HNO_3$, is obtained by mixing solutions of copper nitrate and amidophenylguanidine nitrate; it crystallises in violet prisms, which lose their water of crystallisation ($3H_2O$?) at 100°.

On boiling paratolylhydrazine hydrochloride with cyanamide in alcoholic solution, paratolylamidoguanidine hydrochloride separates, and amidoparatolylguanidine hydrochloride remains in solution; on shaking the dilute acid solution of the latter salt with benzaldehyde, filtering, and adding potassium or sodium nitrate, *benzylideneamidoparatolylguanidine nitrate*, $NH_2\cdot C(NH)\cdot N(C_7H_7)N\colon CHPh,HNO_3$, separates as an oil, which ultimately solidifies. It crystallises in hard, transparent, monosymmetric prisms, melting at 214°, and is sparingly soluble in cold water or alcohol;

$$a : b : c = 1.1659 : 1 : 0.8851.\ \beta = 62°24'.$$

The *picrate*, $C_{15}H_{16}N_4,C_6H_3N_3O_6$, crystallises in yellow needles, melting

at 218°, and is sparingly soluble in water or alcohol. The free *base* is obtained as an oil, which soon crystallises, and is soluble in water, alcohol, benzene, or ether.

Amidoparatolylguanidine, $NH_2\cdot C(NH)\cdot N(C_7H_7)\cdot NH_2$, is prepared by boiling the nitrate of its benzylidene derivative with water until benzaldehyde is no longer eliminated. The *nitrate* is obtained in large, white crystals, melting at 110°, and is very soluble in water or alcohol; it combines with benzaldehyde, giving the benzylidene derivative described above, and on treatment with copper nitrate and sodium acetate gives *copper amidoparatolylguanidine nitrate*, which crystallises in sparingly soluble violet needles. The free *base* is obtained as an oil, which soon crystallises; it reduces hot Fehling's solution or ammoniacal silver nitrate.

Phenylamidoguanidine nitrate, $NH_2\cdot C(NH)\cdot NPh\cdot NH_2,HNO_3$, crystallises in needles melting at 178°; it is only sparingly soluble in water or alcohol, and does not combine with benzaldehyde or yield a violet double salt with cupric nitrate. The *picrate* crystallises in yellow needles, melting at 193°, and is sparingly soluble in water or alcohol.

W. J. P.

Are Diphenyliodonium and Thallium Nitrates Isomorphous? By ARTHUR A. NOYES and C. W. HAPGOOD (*Chem. News*, 1896, **74**, 217).—Saturated solutions of thallous nitrate in water and of diphenyliodonium nitrate in a moderately strong aqueous solution of diphenyliodonium hydroxide were mixed in different proportions, and allowed to crystallise, to a certain extent, in a vacuum; the two salts crystallised out separately, therefore no mixed crystals indicating isomorphism were obtained.

D. A. L.

Chlorophosphines of the Aromatic Series, and their Derivatives. By C. A. AUGUST MICHAELIS (*Annalen*, 1896, **293**, 193—259. Compare Abstr., 1894, i, 586).—Phenylchlorophosphine has been already described (*Annalen*, 1876, **181**, 265), and has given rise to numerous derivatives; the bromophosphine is also known.

[With HUBERT GLAUBITZ].—*Phenylcyanophosphine*, $PPh(CN)_2$, is obtained by the action of phenylchlorophosphine on silver cyanide at ordinary temperatures, and forms a viscous, colourless liquid, which boils at 144—145° under a pressure of 20 mm.; it is indifferent towards water, but dissolves in dilute alkalis, forming alkali cyanide and alkali phenylphosphinite. *Phenylthiocyanophosphine*, $PPh(CNS)_2$, arises from the action of phenylchlorophosphine on silver thiocyanate; it is a viscous, yellow liquid, which boils at 205—207° under a pressure of 20 mm.

[With KUHLMANN.]—The *diamide* of phenylphosphinic acid,

$$PPhO(NH_2)_2,$$

is produced by the action of concentrated aqueous ammonia on phenyloxychlorophosphine, and crystallises from alcohol in white, lustrous leaflets, melting at 189°.

[With JUNKER.]—The *dianilide* crystallises in white needles, with a bluish tinge, and melts at 211°. *Aniline-n-phenylphosphinic acid*,

NHPh·PPhO·OH (compare Michaelis, Abstr., 1894, i, 586), is obtained by heating dry aniline hydrochloride with phenyloxychlorophosphine (1 mol.) for 6 hours at 150°, then heating the mixture of chloride and anilide with dilute ammonia, and acidifying with dilute hydrochloric acid; it forms a white, crystalline powder, and melts at 125°. Concentrated hydrochloric acid resolves it into aniline hydrochloride and phenylphosphinic acid. The *phenylic* salt is obtained by the action of phenol on the mixture of chloride and anilide, and forms small, yellowish-white crystals; it melts at 83°, and boils at 235° under a pressure of 25 mm. The *phenylhydrazide* of phenylphosphinic acid, $PPhO(NH\cdot NHPh)_2$, is produced by the action of phenyloxychlorophosphine on phenylhydrazine, and crystallises from alcohol in white needles, which melt at 175°; it is indifferent towards cold Fehling's solution, but reduces it when heated.

[With G. Schlüter.]—*Phenylmethylphosphinic acid*, PMePhO·OH, crystallises from water in white needles, and melts at 133°; it is formed on distilling phenyldipiperidinemethylphosphonium hydroxide (compare Abstr., 1895, i, 682), piperidine being eliminated. The *silver* salt crystallises in lustrous leaflets, and dissolves sparingly in water; it rapidly becomes brown when exposed to light.

[With O. Holle].—*Phenylhydroxyethylphosphinic acid*,

HO·CHMe·PPhO·OH,

is obtained by the action of phenylchlorophosphine on acetaldehyde (1 mol.), and crystallises in stellar aggregates of needles, melting at 104°; the *barium* salt crystallises in silky needles. *Phenylhydroxybenzylphosphinic acid*, HO·CHPh·PPhO·OH, obtained from phenylchlorophosphine and benzaldehyde, melts at 112—114°; the *barium* salt crystallises in small, lustrous plates, and contains $1H_2O$.

[With Wilhelm Maecker.]—*Parachlorophenylchlorophosphine* (*parachlorophosphenylic chloride*), $C_6H_4Cl\cdot PCl_2$, is produced by the action of phosphorus trichloride on chlorobenzene under the influence of aluminium chloride; it is a liquid having the sp. gr. = 1·425 at 17°, and boils at 253—255°. When heated with bromine and water for 2 hours at 150°, it is converted into 1 : 4-chlorobromobenzene and phosphoric acid. Dry chlorine gives rise to *parachlorophosphenylic tetrachloride*, $C_6H_4Cl\cdot PCl_4$, a yellow, hygroscopic, crystalline substance, which resembles phosphorus pentachloride; water converts it into chlorophosphenylic oxychloride, phosphinic acid being ultimately formed. *Parachlorophosphenylic bromochloride*,

$$C_6H_4Cl\cdot PCl_2Br_2,$$

is obtained by the action of dry bromine on parachlorophosphenylic chloride, and melts at 216°; it fumes in the air, and is converted by water into parachlorophenylphosphinic acid. *Parachlorophosphenylic oxychloride*, $C_6H_4Cl\cdot POCl_2$, is formed from the tetrachloride when the liquid is treated with sulphurous anhydride, and subsequently distilled; it is a pale yellow liquid, having the sp. gr. = 1·4892 at 20°, and boils at 284—285°.

Parachlorophenylphosphinous acid, $C_6H_4Cl\cdot PHO\cdot OH$, is produced when parachlorophenylchlorophosphine is added drop by drop to water,

hydrogen chloride being eliminated, and crystallises from the solution in long, slender needles or lustrous leaflets, and from alcohol in transparent, quadratic leaflets; it melts at 130—131°, reduces silver solution, and forms a white precipitate with ferric chloride. The *ammonium* salt is deposited from water in lustrous leaflets, and the *barium* salt also forms leaflets containing $1H_2O$; the *copper* salt is blue, and contains $4H_2O$; and the *phenylhydrazine* salt crystallises from dilute, aqueous solutions in long, golden yellow needles, melting at 169°.

Parachlorophenylphosphinic acid, $C_6H_4Cl{\cdot}PO(OH)_2$, is readily obtained from parachlorophosphenylic tetrachloride and oxychloride by the action of water, the liquid being then evaporated; it crystallises from water in aggregates of silky needles, separating from alcohol in transparent, quadratic plates and melts at 184—185°. The *hydrogen barium* salt forms lustrous, white needles, the *silver* salt is amorphous, and darkens when exposed to light, and the *hydrogen silver* salt crystallises in lustrous leaflets. The *anhydride* (*phosphinoparachlorobenzene*), $C_6H_4Cl{\cdot}PO_2$, is obtained by heating the finely powdered phosphinic acid with the oxychloride and dry benzene for 2 hours, and forms a white, crystalline powder, which melts at 211°; under the influence of water, it passes into the phosphinic acid.

[With LUDWIG EIFLER.]—*Nitroparachlorophenylphosphinic acid*,

$$NO_2{\cdot}C_6H_3Cl{\cdot}PO(OH)_2,$$

is produced by the action of fuming nitric acid on the foregoing phosphinic acid, and crystallises from that agent in long, slender needles; it also forms white, lustrous leaflets, with a pale, yellowish-green reflex. It is soluble in water, and fuses in the hot liquid, but the melting point of the dry substance is 166—168°. The *ammonium* and *potassium* salts are crystalline, the *sodium* salt crystallises in lustrous, yellowish needles, and contains $6H_2O$, and the *barium* salt forms leaflets containing $2H_2O$; the *calcium* and *silver* salts are amorphous and anhydrous. *Amidoparachlorophenylphosphinic acid*,

$$NH_2{\cdot}C_6H_3Cl{\cdot}PO(OH)_2,$$

is obtained on reducing the nitro-acid with tin and hydrochloric acid, and crystallises from water in beautiful, lustrous needles; it is insoluble in alcohol and ether, and melts, decomposing, above 270°. The *barium* salt crystallises in colourless leaflets, and contains $1\frac{1}{2}H_2O$; the *silver* salt is a white, amorphous substance, insoluble in water.

Parachlorophenylphosphine, $C_6H_4Cl_4{\cdot}PH_2$, obtained by distilling parachlorophenylphosphinous acid in an atmosphere of carbonic anhydride, is a white, crystalline mass, which melts at 17° and boils at 198—200°; it becomes oxidised on exposure to air, forming chlorophenylphosphinous acid, and the same compound is produced under the influence of potash. The *platinochloride* is a yellow, crystalline powder, which does not melt below 270°; the *diethyl* derivative boils at 255—257°; and is a colourless liquid with a penetrating odour. The *methiodide* of the latter is a snow-white, deliquescent powder, and melts at 97—98°. *Parachlorophosphenylic chloride phenylhydrazone*,

$$C_6H_4Cl{\cdot}P{:}N{\cdot}NHPh,$$

is obtained from the chloride and phenylhydrazine in ethereal solution; it crystallises from benzene in white, lustrous leaflets, and melts and decomposes at 161°.

[With Erich Gundermann.]—*Parabromophenylchlorophosphine* (*parabromophosphenylic chloride*), $C_6H_4Br\cdot PCl_2$, is prepared from bromobenzene and phosphorus trichloride under the influence of aluminium chloride, and forms a somewhat viscous, highly refractive liquid, having a sp. gr. = 1·6895 at 15°; it boils at 271—272°, and when heated with bromine and water yields paradibromobenzene. The *tetrachloride*, obtained by the action of chlorine, is a yellow, crystalline substance, which melts at 55°; the *oxychloride* boils at 290—291°.

Parabromophenylphosphinous acid, $C_6H_4Br\cdot PHO\cdot OH$, is produced by the action of water on the foregoing chlorophosphine, and crystallises from dilute alcohol in large, white leaflets; it is sparingly soluble in cold water, and melts at 143°. The *potassium* salt forms colourless, quadratic plates, and the *ammonium* salt crystallises in lustrous, white leaflets; the *calcium* salt is deposited from water in crystalline aggregates, and the *barium* salt forms white leaflets containing $1H_2O$. The *lead* and *copper* salts are anhydrous, the *aniline* salt crystallises from water in prisms, and the *phenylhydrazine* salt forms large, lustrous leaflets, which melt and decompose at 181°.

Parabromophenylphosphinic acid, $C_6H_4Br\cdot PO(OH)_2$, is obtained by treating the oxychloride with hot water, hydrogen chloride being eliminated; it crystallises in long, lustrous needles, and melts at 202°, yielding metaphosphoric acid and bromobenzene when heated above this temperature. The *hydrogen potassium* salt crystallises in needles, and the *hydrogen barium* salt in white, lustrous leaflets, which contain $1H_2O$; the *silver* salt is amorphous, and the *hydrogen silver* salt resists the action of light, and crystallises in lustrous, white leaflets. The *anhydride* (*phosphinobromobenzene*), $C_6H_4Br\cdot PO_2$, is obtained by heating the acid with the oxychloride and benzene until hydrogen chloride is no longer liberated; it is a white powder which melts at 185—186°, and is converted into the acid under the influence of water.

An *isomeride* of parabromophenylphosphinic acid has been isolated from the residue containing aluminium chloride, after separation of the bromophenylchlorophosphine; it crystallises in long, white, lustrous needles, and melts at 265°. The *silver* salt is a white, amorphous powder.

Nitroparabromophenylphosphinic acid, $NO_2\cdot C_6H_3Br\cdot PO(OH)_2$, is produced by the action of fuming nitric acid on bromophenylphosphinic acid, and crystallises in yellow leaflets; it melts at 185°, and when strongly heated, becomes ignited and chars. The *silver* salt is a white powder.

Parabromophenylphosphine, $C_6H_4Br\cdot PH_2$, is formed when parabromophenylphosphinous acid is distilled in an atmosphere of carbonic anhydride; it is a colourless, crystalline mass, which melts at 40° and boils at 195—196°. The *platinochloride* is bright yellow. The *diethyl* derivative boils at 265°, and is a colourless liquid of disagreeable and penetrating odour; the *methiodide* of this substance crystallises in white needles, and melts at 135°, whilst the *ethiodide*, which also forms white needles, melts at 165°. The *phenylhydrazone* of parabromophosphenylic chloride, $C_6H_4Br\cdot P\!:\!N\cdot NHPh$, is obtained from

the chloride and phenylhydrazine; it separates from benzene in small crystals, and melts at 160°.

[With J. RABINERSON, R. KATZENSTEIN, and PH. KUNZ.]—Paramethoxyphenylchlorophosphine (paranisylchlorophosphine) is obtained by heating methoxybenzene with phosphorus trichloride and commercial aluminium chloride during 4—6 hours (compare Abstr., 1894, i, 586); it is a colourless, highly refractive liquid, having the sp. gr. = 1·0764 at 15°, and boils at 245—253° under a pressure of 12—15 mm. *Anisyltetrachlorophosphine*, $OMe \cdot C_6H_4 \cdot PCl_4$, is produced by the action of chlorine, and melts at 35—40°; *anisyloxychlorophosphine*, $OMe \cdot C_6H_4 \cdot POCl_2$, is obtained from the tetrachloride by means of sulphurous anhydride, and forms a viscous, yellowish liquid, which boils at 173° under a pressure of 12—15 mm.

Anisylphosphinous acid, $OMe \cdot C_6H_4 \cdot PHO \cdot OH$, is produced by the action of water on the chlorophosphine, and crystallises in long, slender, lustrous needles, melting at 112°; the *lead* salt forms lustrous scales, and the *phenylhydrazine* salt crystallises from hot water in beautiful, nacreous leaflets, and melts at 116°.

Anisylphosphinic acid, $OMe \cdot C_6H_4 \cdot PO(OH)_2$, is formed when the oxychloride is heated with water until hydrogen chloride ceases to be evolved; it separates from water in large crystals, and melts at 158°. The *hydrogen potassium* salt contains $1H_2O$, the *hydrogen barium* salt is anhydrous, and the *copper* and *silver* salts are also anhydrous; the *ferric* salt is yellow, and contains $3H_2O$, whilst the *nickel* and *hydrogen lead* salts are anhydrous. The *phenylhydrazine* salt crystallises from water. The *anhydride* (*phosphinoanisoïl*), $OMe \cdot C_6H_4 \cdot PO_2$, is a white, amorphous powder, and melts at 52°.

Nitranisylphosphinic acid, $NO_2 \cdot C_6H_3(OMe) \cdot PO(OH)_2$, is obtained by the action of fuming nitric acid on anisylphosphinic acid, and crystallises from alcohol in slender, colourless needles, melting at 187°; the *hydrogen barium* salt contains $3H_2O$, whilst the *copper* and *basic cobalt* salts are anhydrous.

Anisyldiethylphosphine, $OMe \cdot C_6H_4 \cdot PEt_2$, prepared from the chlorophosphine and zinc ethide, is a colourless liquid having the sp. gr. = 0·9978 at 18°, and boils at 266—267°; the *methiodide* melts at 91°, and the *platinochloride* of the corresponding methochloride crystallises in beautiful, brownish prisms, and melts at 142°. The *ethiodide* crystallises in long, colourless needles, and melts at 65°; the *platinochloride* of the corresponding ethochloride forms bright brown crystals, and melts at 148°.

[With R. KATZENSTEIN.]—Para-ethoxyphenylchlorophosphine (paraphenetylchlorophosphine), $OEt \cdot C_6H_4 \cdot PCl_2$, prepared from ethoxybenzene, phosphorus trichloride, and aluminium chloride, is a colourless liquid which boils at 266°.

Phenetylphosphinous acid, $OEt \cdot C_6H_4 \cdot PHO \cdot OH$, is obtained by the action of water on the chlorophosphine, and crystallises in white, lustrous leaflets, melting at 115°. *Phenetylphosphinic acid*,

$$OEt \cdot C_6H_4 \cdot PO(OH)_2,$$

prepared from the tetrachloride, crystallises in white needles, and melts at 165°; the *silver* salt is a white, crystalline substance.

Phenetyldiethylphosphine, $OEt\cdot C_6H_4\cdot PEt_2$, is a colourless liquid which boils at 275°, and has a disagreeable odour; the *methiodide* melts at 60°, and the *platinochloride* of the corresponding methochloride crystallises from water in needles, and melts at 208°. M. O. F.

Derivatives of Metadi-iodoparahydroxybenzaldehyde. By CARL PAAL and L. MOHR (*Ber.*, 1896, 29, 2302—2307. Compare Abstr., 1896, i, 40).—Metadi-iodoparahydroxybenzaldehyde forms well-defined alkali derivatives. The *sodium* derivative crystallises from water in long, white needles, and is sparingly soluble in aqueous alkalis, ethylic alcohol, and methylic alcohol; the *silver* derivative is a yellowish powder which dissolves readily in ammonia, but is insoluble in water.

Metadi-iodoparahydroxybenzoic acid, $OH\cdot C_6H_2I_2\cdot COOH$, first obtained by Peltzer (*Annalen*, 146, 294), is produced on oxidising metadi-iodoparahydroxybenzaldehyde with alkaline potassium permanganate; it crystallises from alcohol in white needles, and melts at 237°.

Metadi-iodoparahydroxybenzaldoxime, $OH\cdot C_6H_2I_2\cdot CH{:}NOH$, crystallises from alcohol in white needles, and melts at 203°; it is a stable compound, and has not been converted into the nitrile. *Metadi-iodoparahydroxybenzylidenephenylhydrazone*, $OH\cdot C_6H_2I_2\cdot CH{:}N\cdot NHPh$, crystallises from alcohol in yellow needles, and melts at 160°. *Metadi-iodoparahydroxybenzylideneaniline*, $OH\cdot C_6H_2I_2\cdot CH{:}NPh$, crystallises from alcohol in beautiful violet plates, having metallic lustre; it contains 1 mol. C_2H_6O, which is lost at 100°, and it melts at 169°. *Metadi-iodoparahydroxybenzylideneparatoluidine* crystallises in blue leaflets having metallic lustre, and melts at 189°. *Metadi-iodoparahydroxybenzylidene-α-naphthylamine* forms orange plates melting at 156°, and *metadi-iodoparahydroxybenzylidene-β-naphthylamine* separates from alcohol in red crystals, and melts at 165°.

Metadi-iodoparahydroxybenzylideneacetone, $OH\cdot C_6H_2I_2\cdot CH{:}CH\cdot COMe$, is obtained by the action of acetone on the aldehyde under the influence of concentrated caustic soda; it crystallises in aggregates of white needles, and melts at 168°.

Metadi-iodoparahydroxycinnamic acid, $OH\cdot C_6H_2I_2\cdot CH{:}CH\cdot COOH$, is formed when metadi-iodoparahydroxybenzaldehyde is heated with acetic anhydride and anhydrous sodium acetate for 10—12 hours at 130—140°; it crystallises from ethylic acetate in lustrous, white needles, and melts at 245°. The *silver* salt is a white powder, insoluble in water; the *methylic* salt crystallises from alcohol in small, white needles, and melts at 107°. M. O. F.

New Derivatives of Parahydroxybenzaldehyde, of Paracyanophenol and of Parahydroxybenzoic Acid. By KARL AUWERS and JULIUS REIS (*Ber.*, 1896, 29, 2355—2360. Compare Paal, Abstr., 1895, i, 40 and 225).—3 : 5 : 4-*Dichlorohydroxybenzaldehyde*, obtained by passing dry chlorine into an acetic acid solution of the hydroxyaldehyde, crystallises in colourless needles, melts at 156°, and is sparingly soluble in benzene, chloroform and light petroleum but readily in alcohol, ether and ethylic acetate. In order to prepare the substituted para-cyanophenols the corresponding substituted hydroxy-

aldehydes were converted into their oximes and the latter on boiling for 2 hours with acetic anhydride were converted into the acetyl derivatives of the hydroxy-nitriles.

3 : 5 : 4-*Di-iodohydroxybenzaldoxime* crystallises in small, colourless needles and melts at 192°. It is readily soluble in most organic solvents, only sparingly, however, in ether and light petroleum.

3 : 5 : 4-*Dichlorhydroxybenzaldoxime* melts at 185° ; it is readily soluble in alcohol, ether, and ethylic acetate, sparingly soluble in benzene and chloroform and insoluble in light petroleum.

3 : 4-*Bromacetoxybenzonitrile* crystallises in colourless needles and melts at 100—101°.

The following compounds have also been prepared.

3 : 5 : 4-*Dichloracetoxybenzonitrile*, melting at 93° ; 3 : 5 : 4–*Dibromacetoxybenzonitrile*, melting at 150°, and the corresponding *di-iodo* compound, melting at 198°.

3 : 4-*Bromohydroxybenzonitrile*, melting at 155° ; 3 : 5 : 4-*dichlorohydroxybenzonitrile*, melting at 146° ; the corresponding *dibromnitrile*, melting at 187°, and *di-iodonitrile*, melting at 205—206°. These compounds were obtained by hydrolysing the acetyl derivatives with 4 per cent. alcoholic solution of sodium.

Methylic 3 : 4-*bromohydroxybenzoate* distils at 163—166° under 16 mm. pressure and melts at 107°.

Methylic 3 : 5 : 4-*dibromohydroxybenzoate* melts at 125° and *methylic* 3 : 5 : 4 *di-iodohydroxybenzoate* melts at 167°. J. J. S.

Derivatives of Piperonal. By CARL GOLDSCHMIDT (*Ber.*, 1896, **29**, 2328).—*Piperonalphenylmethylhydrazone* is formed when molecular quantities of piperonal and *as*-phenylmethylhydrazine are heated together in an oil bath at 150° ; it consists of white needles, melting at 85°, and is insoluble in water and non-poisonous.

Piperonalparaphenetidine, produced in an analogous manner, forms white, glistening plates melting at 105°. It is insoluble in water, and is only very slightly poisonous. J. F. T.

Regularities in the Behaviour of the Di-ortho-substituted Aromatic Carbonyl Compounds. By VICTOR MEYER and G. PAVIA (*Ber.*, 1896, **29**, 2564—2569).—From experimental data the following law is formulated. "That double acetylation takes place almost quantitatively when both acetyl groups must enter between two ortho-methyl groups, but acetylation does not occur when this cannot be the case; when one acetyl group can enter between two such methyl groups, although from the constitution of the hydrocarbon it is not necessary that it should do so, further acetylation will occur only to a limited extent."

From this it follows that, in a compound containing an acetyl group in the ortho-position relatively to two methyl groups, a further acetyl group can be made to enter.

Benzene, acetophenone, and ortho- or para-xylene do not under any circumstances yield diacetyl derivatives ; metaxylene gives about 2·3 per cent. of the diacetyl compound, although on repeating the operation several times a large quantity of this compound can be obtained.

From this it would appear that in the acetylation of metaxylene, a small quantity of the compound [Me_2 : Ac = 1 : 3 : 2] is produced.

2 : 4-*Diacetylmetaxylene*, $C_6H_2Me_2Ac_2$, forms slender, white needles melting at 108° and boiling at 306°. Mesitylene, durene and isodurene are instances in which an acetyl group can only enter in the ortho-position to two methyl groups, these compounds, therefore, yield on further acetylation 100 per cent. of the diacetyl derivative.

Since the acetyl compound of pseudocumene cannot be further acetylated, it would follow that in the acetylation of pseudocumene, the acetyl group does not enter in position 2.

Symmetrical triethylbenzene and ethylmesitylene readily yield diacetyl derivatives.

It is therefore possible by this means to ascertain quickly and with small quantities of substance whether tri- or tetra-alkylated benzene derivatives are substituted in the positions 1 : 3 : 5 or not.

The authors incline to the opinion that mesitylene obtained from acetone is a homogeneous substance and is not admixed with hemellithene.

Mesitylene is completely converted into its diacetyl derivative, whilst hemellithene only yields a monacetyl compound. No fraction of the "mesitylene from acetone" could be obtained which did not yield a diacetyl derivative. Mesitylene is only first partly transformed into an isomeride on carboxylation; a similar instance has been previously noticed in the carboxylation of durene. J. F. T.

Formation of Ethereal Salts. By RUDOLF WEGSCHEIDER (*Ber.*, 1896, **29**, 2301).—In connection with a recent discussion of Victor Meyer's law, by Angeli, the author points out that identical views were formulated by him in an investigation of hemipinic acid and its ethereal salts (Abstr., 1895, i, 420; compare also i, 499). The publications in question had not met the notice of Angeli.

M. O. F.

Durenecarboxylic Acids. By VICTOR MEYER and LOTHAR WÖHLER *Ber.*, 1896, **29**, 2569—2573).—It is found that by avoiding an excess of aluminium chloride and by working quickly, no intramolecular rearrangement ensues when durene is converted into its carboxylic acids by Gattermann's method.

It is further shown that the three durenecarboxylic acids behave in accordance with the law of etherification, namely, that the acids of durene and iso-durene which contain the group $\begin{matrix}CMe\\CMe\end{matrix}>C\cdot COOH$ give no ethylic salt when treated by E. Fisher's method, whilst the carboxylic acid of prehnitol containing the group $\begin{matrix}CH\\CMe\end{matrix}>C\cdot COOH$ is converted quantitatively into the ethylic salt under these conditions.

Durenecarboxylic acid, which has never before been obtained possessing an absolutely sharp melting point, has now been purified by converting it into the methylic salt (m. p. 58°) and rehydrolysis. The acid prepared in this way melts quite sharply at 176·5°, and on distillation with lime yields pure durene (m. p. 78°). J. F. T.

Action of Ammonia on Alkylic Phenyldibromopropionates. By H. BAUCKE (*Rec. Trav. Chim.*, 1896, **15**, 128—134).—Ethylic phenyldibromopropionate, CHPhBr·CHBr·COOEt, when heated to 45° in sealed vessels for about 2 hours with an excess of aqueous ammonia, previously saturated at 0° with ammonia, yields a small quantity of Anschütz and Selden's bromocinnamamide, $CHPh\colon CBr\cdot CO\cdot NH_2$ (Abstr., 1887, 829), melting at 118°, together with larger quantities of *ethylic monobromocinnamate*. The mixture is best separated by dissolving it in benzene and adding light petroleum when the amide separates in the form of small crystals, whilst the mother liquor on evaporation yields the ethylic salt which distils at 179—180° (28 mm. pressure); this, when hydrolysed with alcoholic potash, yields a mixture of α-bromocinnamic acid (m. p. 120°) and allo-α-bromocinnamic acid (m. p. 131°).

When ethylic phenyldibromopropionate and aqueous ammonia are heated together under the same conditions, but for a longer time, namely, about 3 days, the only product is *α-amidocinnamamide*, $CHPh\colon C(NH_2)\cdot CO\cdot NH_2$, which crystallises from ethylic alcohol, in which it is readily soluble, in rhombic plates and melts at 172°. When hydrolysed, it yields an *acid* melting at 160°; this has not been further investigated.

The author shows, in conclusion, that the bromocinnamamide melting at 118°, is, most probably, a derivative of α-bromocinnamic acid (m. p. 120°) and not of the α-allo acid, and also that the α-amidocinnamide is to be regarded as a derivative of the same acid. J. J. S.

Phenylpropiolamide. By H. BAUCKE (*Rec. Trav. Chim.*, 1896, **15**, 123—127).—*Phenylpropiolamide* is best obtained by mixing methylic or ethylic phenylpropiolate (Liebermann and Sachse, Abstr., 1891, 1483) with an excess of aqueous ammonia, saturating the mixture with gaseous ammonia at −3°, and keeping it in sealed tubes at 8° for 30 hours. When recrystallised from boiling water, it melts at 102° (compare Stockhausen and Gattermann, Abstr., 1893, i, 164). If treated with a solution of potassium hypobromite, it yields the *potassium* derivative of the *bromamide*, CPh⋮C·CO·NKBr, the solution of which when treated with cooled 1 per cent. acetic acid gives a white precipitate of *phenylpropiolbromamide*. The *silver* salt also forms a white precipitate.

All attempts to convert this bromamide into the amine, $CPh⋮C\cdot NH_2$, by means of alkalis proved futile. J. J. S.

Phenylcoumalin. By FERRUCCIO SEVERINI (*Gazzetta*, 1896, **26**, ii, 326—350).—The author has examined the supposed α-phenylcoumalin isolated from coto bark by Ciamician and Silber (Abstr., 1894, i, 300), and shows it to be really α-phenylcoumalin, $CH{\lessdot}\genfrac{}{}{0pt}{}{CH\cdot CPh}{CH\colon CO}{>}O$; it is obtained as a yellowish microcrystalline powder, which has an aromatic odour, and melts at 68°. When heated in sealed tubes, at 110° with concentrated hydrochloric acid, it is converted into a *polymeride* $(C_{11}H_8O_2)_2$, which forms a white, crystalline powder melting and decomposing at 219°; its molecular weight was determined by the cryoscopic method

in benzoic acid solution. Phenylcoumalin yields phenylvaleric acid on reduction with sodium amalgam.

Phenylcoumalin picrate, $C_{11}H_8O_2,C_6H_2(NO_2)_3\cdot OH$, crystallises in beautiful, yellow, anorthic crystals melting at 81—82°; $a:b:c = 1\cdot3443:1:1\cdot7030$. $\alpha = 107°17'$, $\beta = 114°14'$, $\gamma = 63°30'$. Cryoscopic determinations show it to be dissociated in acetic acid solution, just as are the picrates of cotoïn and the dihydroxybenzenes. The *salicylate*, $C_{11}H_8O_2,C_6H_4(OH)\cdot COOH$, is obtained in colourless crystals melting at 93°.

Phenyldimethylcoumalin combines with quinol, giving a white, flocculent crystalline *substance*, $C_{13}H_{12}O_2,C_6H_4(OH)_2$, melting at 113°, and when heated in a closed tube with concentrated hydrochloric acid is partly converted into a resinous mass.

Phenylcoumalin combines with boiling aniline giving a *compound* of the composition $C_{11}H_8O_2,2NH_2Ph$; this crystallises from benzene in white needles which melt at 115—118°, and contain benzene of crystallisation, whilst from alcohol it is obtained in pyramids melting at 142°. On boiling the aniline compound with concentrated hydrochloric acid, it is quantitatively converted into 1 : 2-*diphenyl*-6-*pyridone*, $NPh<\substack{CO\cdot CH \\ CPh:CH}>CH$, which crystallises in white needles, melting at 144—146°; it is insoluble in water, but very soluble in benzene.

2-*Phenyl*-6-*pyridone*, $NH<\substack{CO—CH \\ CPh:CH}>CH$, may be prepared by boiling phenylcoumalin with ammonium acetate and glacial acetic acid; it crystallises in yellow scales melting at 197° and is soluble in hot water or alcohol, but insoluble in ether. Its *hydrochloride* crystallises in yellow needles melting at 104°, and, together with the platinochloride and aurochloride, is decomposed by water. On distilling 2-phenyl-6-pyridone with zinc dust, it yields 2-phenyl-6-pyridine; the picrate of the latter melts at 175°, and the *platinochloride* crystallises with $2H_2O$ in yellow needles melting at 204°. The pyridone is converted into 6-*chloro*-2-*phenylpyridine* on heating in a closed tube with phosphorus trichloride for 6 hours at 150°; it crystallises in white needles melting at 34°, and has an odour resembling that of pyridine. The platinochloride and aurochloride are crystalline. W. J. P.

Phenylcoumalin. By OSWALD HESSE (*Ber.*, 1896, **29**, 2322—2323).—A reply to Leben (Abstr., 1896, i, 574.) The author affirms the accuracy of the melting point, 61—62°, he gave for phenylcoumalin; the higher melting point (68°) of Ciamician and Silber must be due to some error. J. F. T.

[Phenylcoumalin.] By GIACOMO L. CIAMICIAN and PAUL G. SILBER. (*Ber.*, 1896, **29**, 2659—2662).—A reply to Hesse (preceding abstract). The authors maintain the correctness of the melting point they originally assigned to phenylcoumalin, and draw attention to the uncertainty of the methods used by Hesse to establish the purity of his substance. A. L.

Decomposition of the Phenolic Acids derived from Benzene and Naphthalene. By PAUL CAZENEUVE (*Bull. Soc. Chim.*, 1896,

[3], **15**, 72—82).—The fatty acids and the carboxylic acids derived from cycloid hydrocarbons, when heated with aniline, give rise to anilides. When, however, phenolic hydroxyl groups are present, the compounds tend to decompose into carbonic anhydride and the phenol from which they are derived. Further, the phenolic acids decompose more easily in the presence of aniline than under the same conditions in the presence of water. From the results of his experiments, the author deduces the following laws.

(1) The stability of the carboxyl group in the phenolic acids decreases with the number of hydroxyl groups present in the molecule; the stability is further decreased by the introduction of halogen atoms.

(2) Phenolic acids most easily decompose when the hydroxyl is in the ortho-position, the metahydroxy-acids are the most stable. In the case of dicarboxylic acids, the carboxyl group in the meta-position is the least easily broken off.

(3) Ethereal salts are more stable than the acids themselves; displacement of the hydrogen of hydroxyl by a radicle has the same effect. M. W. T.

Bromoprotocatechuic Acid and the three Isomeric Bromoveratric and Nitroveratric Acids. By E. C. THEODOR ZINCKE and BRUNO FRANCKE (*Annalen*, 1896, **293**, 175—193).—Protocatechuic acid is most conveniently brominated in glacial acetic acid solution, the initial product being 5-bromoprotocatechuic acid, whilst excess of the halogen converts it into tribromocatechuic acid and tetrabromocatechol; hydriodic acid and phosphorus reduce the bromo-derivative to the original acid, and concentrated nitric acid oxidises it to dibromo-β-naphthaquinone-2-carboxylic acid. *Diacetylbromoprotocatechuic acid* is obtained by heating it with acetic chloride in sealed tubes; it crystallises from water in small, white needles, and melts at 187°. The *methylic* salt of bromoprotocatechuic acid crystallises from methylic alcohol, and melts at 201—202°.

5-*Bromoveratric acid*, $COOH\cdot C_6H_2Br(OMe)_2$, is obtained in the form of its methylic salt when methylic bromoprotocatechuate is heated with methylic iodide and sodium methoxide; it is also formed when nitroveratric acid is reduced with tin and concentrated hydrobromic acid. It crystallises from methylic alcohol or glacial acetic acid, and melts at 191°; the *methylic* salt crystallises in beautiful, four-sided prisms, and melts at 71—72°.

6-*Bromoveratric acid* was produced by Koelle (*Annalen*, 1871, **159**, 244) and Matsmoto (Abstr., 1878, 502) by the direct bromination of veratric acid, and has been now obtained in the form of its methylic salt by the action of bromine on ethylic veratrate in glacial acetic acid solution, and also by diazotising ethylic 6-amidoveratrate, and treating the product with cuprous bromide; it melts at 183—184°, and the *methylic* salt crystallises from methylic alcohol and melts at 88—89°.

2-*Bromoveratric acid*, obtained by the action of cuprous bromide on diazotised 2-amidoveratric acid (Kuhn, Abstr., 1895, i, 367), crystallises from alcohol, acetone, or glacial acetic acid in needles, and melts at 201—202°; the *methylic* salt is crystalline, and melts at 46°.

The *methylic* salt of 6-amidoveratric acid is formed on reducing the corresponding nitro-compound with tin and hydrochloric acid; it crystallises from benzene in lustrous, monoclinic plates, and melts at 133°.

5-*Nitroveratric acid* is obtained from eugenol by nitration, methylation of the potassium nitro-eugenol first prepared by Weselsky and Benedikt, and subsequent oxidation of this substance; it separates from hot solvents in slender, white needles, and melts at 194°. When this acid is reduced, the resulting amidoveratric acid diazotised, and the liquid heated, hydroxyveratric acid is formed, and may be readily converted into the trimethyl ether of methylic gallate. The *methylic* salt of 5-nitroveratric acid forms slender needles, and melts at 78°; reduction with tin and hydrochloric acid converts it into amidoveratric acid. M. O. F.

Action of Glycocine on Acetophenone-orthocarboxylic Acid. By SIEGMUND GABRIEL and GEORG GIEBE (*Ber.*, 1896, **29**, 2518—2525).—*Methylenephthalimidylacetic acid*,

$$C_6H_4<\genfrac{}{}{0pt}{}{C(CH_2)}{CO\text{———}}>N\cdot CH_2\cdot COOH,$$

obtained by heating glycocine with acetophenonecarboxylic acid in molecular proportion at 160°, crystallises in thick prisms, which melt with effervescence at 199—200°; the *methylic* salt sinters at 102—103°, and melts at 105—106°; the *silver* salt crystallises in beautiful, white needles, and other metallic salts are well defined. When the acid is distilled, methylenephthalomethimidine (Gabriel, Abstr., 1885, 1228) is produced; it is also formed when acetophenonecarboxylic acid is heated with methylamine. The *ethylic* salt of acetophenonecarboxylic acid, which boils at 279°, yields *methylenephthalobenzylimidine*, $C_6H_4<\genfrac{}{}{0pt}{}{C(CH_2)}{CO\text{———}}>N\cdot CH_2Ph$, when heated with benzylamine; this crystallises from ethylic acetate in lustrous prisms, and melts at 122°.

Methylphthalimidineacetic acid, $C_6H_4<\genfrac{}{}{0pt}{}{CHMe}{CO\text{———}}>N\cdot CH_2\cdot COOH$, is formed on reducing methylenephthalimidylacetic acid with sodium amalgam, and when crystallised from water contains $1H_2O$, which is removed on heating at 100°; the anhydrous substance melts at 162—162·5°, and the crystals at 124°. The *silver* salt crystallises in lustrous, white needles. The acid distils in a vacuum without decomposing, but under atmospheric pressure 1′ : 2′-*dimethylphthalimidine*, $C_6H_4<\genfrac{}{}{0pt}{}{CHMe}{CO\text{———}}>NMe$, is produced; its *aurochloride* crystallises in rhombic leaflets and plates, and melts at 163°. This base is also formed when phthalomethimidineacetic acid, $CO<\genfrac{}{}{0pt}{}{C_6H_4}{NMe}>CH\cdot CH_2\cdot COOH$, is distilled.

Benzylphthalimidine, which has been hitherto obtained by reducing benzylidenephthalimidine with phosphorus and hydriodic acid, is also

formed when the amide of deoxybenzoïncarboxylic acid is reduced with sodium amalgam. M. O. F.

A Forgotten Colour Reaction of Gallic Acid and Tannin. By ERICH HARNACK (*Arch. Pharm.*, 1896, **234**, 537—542). When a solution of tannin or gallic acid is made alkaline with potash, and a few drops of lead acetate solution are added, a red precipitate, which is slightly soluble in the reagents, is formed. This reaction was first described by Buchner (*Annalen*, 1845, **53**, 357), and ascribed by him to the formation of tannoxylic acid, the composition of which was found by Gerhardt to be $C_7H_6O_6$. The colouring matter which is formed has not been obtained pure, since it very readily decomposes with evolution of carbonic anydride and formation of a brown substance. The author considers that it is probably either a quinone of gallic acid or the corresponding quinhydrone. A. H.

Suggested Existence of two Orthophthalic Acids. By CARL GRAEBE (*Ber.*, 1896, **29**, 2802—2807. Compare Howe, Abstr., 1896, i, 480).—Following the directions of Howe (*loc. cit.*), the author has failed to obtain more than one modification of orthophthalic acid, and therefore questions the existence of a second form; he points out that the melting point of phthalic acid is indefinite, depending on the rate at which the temperature rises and the quantity of substance employed. Experiments have been made with three specimens of phthalic acid, one of which was obtained from the anhydride by the action of cold caustic soda, another consisting of phthalic acid which had been submitted to prolonged treatment with boiling 30 per cent. caustic soda, whilst the aqueous solution of the third was boiling for several hours; the quantity of each specimen dissolved by 100 parts of absolute alcohol at 18° was approximately the same, amounting in each case to about 11·8 parts.

Hydrogen aniline phthalate is produced on mixing alcoholic solutions of aniline and phthalic acid, the employment of 1, 2, 3 or 4 molecular proportions of the base being without influence on the composition of the product; this is inconsistent with Howe's statement that the aniline salt contains two molecular proportions of the base. It melts at 155°, and at once solidifies, water being eliminated with production of phthalanil; when heated for 20—24 hours at 90°, aniline is removed, and the residue consists solely of phthalic acid, the same result being attained in 4—6 hours at 120—125°.

Hydrogen α-naphthylamine phthalate is obtained from phthalic acid and 1, 2 or 3 molecular proportions of α-naphthylamine, and, contrary to the statement of Howe, the normal salt is not produced; it melts at 159—160°, and undergoes no change at 90—100°. When heated at 115—125° for 36—40 hours, the residue consists solely of phthalic acid, whilst exposure to a temperature of 190° converts it in a few minutes into naphthylphthalimide.

Hydrogen quinoline phthalate affords a fresh instance of disagreement with Howe's observations. This substance, which is not associated with a normal salt, melts at 98—99°; it almost completely volatilises at

90—100°, and loses a certain proportion of quinoline when preserved in the exsiccator.

The author is unable to confirm Howe's observations regarding the production of a dihydrophthalic acid differing from Baeyer's $\Delta^{3:5}$-dihydrophthalic acid. He attributes the results which Howe obtained to the presence of a foreign substance in the phthalic anhydride employed, and points out that when phthalic acid is heated during several hours with 30 per cent. caustic soda, a product is formed which contains benzoic acid, unless deposition of solid matter on the sides of the flask is carefully prevented. M. O. F.

α-Methylphthalic Acid. By OSCAR BLANK (*Ber.*, 1896, **29**, 2376—2381).—*Benzylidenemethylphthalide*, $C_6H_3Me<{C(CHPh) \atop CO\text{———}}>O$, is formed when α-methylphthalic anhydride is heated with phenylacetic acid and sodium acetate. Two isomerides appear to be produced, only one of which has been isolated; this crystallises in slender, light, yellow needles melting at 138°. When this substance is treated in methyl alcoholic solution with sodium methoxide, it passes into 2′:3-*phenylmethyldiketohydrindene*, $C_6H_3Me<{CO \atop CO}>CHPh$, which crystallises in colourless needles, softens at 118°, and melts at 131°. The *sodium* derivative readily reacts with alcoholic halogen derivatives and acid chlorides. 2′:3:2′-*Phenyldimethyldiketohydrindene* crystallises in colourless, rhombic plates melting at 123·5°. 2′:3:2′-*Phenylmethylethyldiketohydrindene* melts at 91—93°. 2′:2′:3-*Phenylbenzylmethyldiketohydrindene* forms colourless rhombic plates, and melts at 120—121°. *Ethylic* 2′:3-*phenylmethyldiketohydrindeneacetate*,

$$C_6H_3Me<{CO \atop CO}>CPh\cdot CH_2\cdot COOEt,$$

forms colourless crystals, melting at 95—96°. When phenylmethyldiketohydrindene is boiled with alcohol for some time, or oxidised by means of nitrous acid, it is converted into *bis-methylphenyldiketohydrindene*, $C_2Ph_2(\colon C_2O_2\colon C_6H_3Me)_2$, which crystallises in white plates, melting at 209—211°. It is also formed when 2′:2′:3-*bromophenylmethyldiketohydrindene* is boiled with alcohol. This bromo-compound is readily obtained by the bromination of the hydrindene in chloroform solution; it crystallises in slender, white needles, and melts at 76—77°. 2′:2′:3-*Anilidophenylmethyldiketohydrindene* is obtained by the action of aniline on the bromo-derivative. It forms golden yellow needles melting at 169°. 2′:3-*Phenylmethyldiketohydrindenedioxime* crystallises in white plates, and melts and decomposes at 204°. A. H.

β-Amido-α-hydrindone. By SIEGMUND GABRIEL and ROBERT STELZNER (*Ber.*, 1896, **29**, 2603—2608).—α-Hydrindone,

$$C_6H_4<{CH_2 \atop CO}>CH_2$$

(Abstr., 1889, 1172), was converted into the oxime by treating it in alcoholic solution with amylic nitrite and hydrochloric acid. This

derivative yields a brownish-yellow *di-phenylhydrazone*, which melts and decomposes at 228—229°, and is different from the isomeric compound prepared by W. Wislicenus and Kötzle from diketohydrindene (Abstr., 1889, 1067); this shows that the oxime really has the formula, $C_6H_4<^{CH_2}_{CO}>C:NOH$, assigned to it by Kipping (Trans., 1894, 492), and not the other possible formula, $C_6H_4<^{C(NOH)}_{CO}>CH_2$. It can be reduced with stannous chloride to *β-amido-α-hydrindone*, the *hydrochloride* of which darkens at about 200° and decomposes at 230—240°, whilst the *picrate* decomposes at 152°, and the *platinochloride* darkens at about 200°; the base itself is obtained, more or less impure, as a dark violet powder. When an aqueous solution of the hydrochloride is evaporated with potassium thiocyanate, *orthobenzyleneiminazolylmercaptan*,

$$\begin{matrix} CH_2-C-N \\ | \quad\quad \| \\ C_6H_4\cdot C\cdot NH \end{matrix}>C\cdot SH \quad \text{or} \quad \begin{matrix} CH_2-C\cdot NH \\ | \quad\quad \| \\ C_6H_4\cdot C—N \end{matrix}>C\cdot SH,$$

is formed; this decomposes at about 280°.

Amidohydrindone hydrochloride does not react in a similar way with potassium cyanate; it simply yields *α-hydrindonyl-β-carbamide*, $C_6H_4<^{CH_2}_{CO}>NH\cdot CO\cdot NH_2$, which melts and decomposes at 210—211°.

C. F. B.

α-Methylphthalide and Orthoethylbenzoic Acid. By GEORG GIEBE (*Ber.*, 1896, **29**, 2533—2543).—Orthoethylbenzoic acid (compare Gabriel and Michael, Abstr., 1878, 427) is obtained by heating methylphthalide with yellow phosphorus and hydriodic acid for 60—65 hours at 137°; it crystallises in long needles, melts at 68°, and boils at 259° under a pressure of 760 mm. The *copper* salt is anhydrous, and the calcium salt contains $3H_2O$; the *ethylic* salt boils at 231° under a pressure of 763 mm., and the *chloride* at 219° under a pressure of 744·5 mm. The *amide* crystallises from water in long white needles, and melts at 151—153°, the *ureïde* melts at 197—198°, and the *nitrile* boils at 212°; *orthoethylthiobenzamide* crystallises from light petroleum in long colourless needles, and melts at 78—79°.

5 : 2-*Nitroethylbenzoic acid*, obtained from ethylbenzoic acid and a mixture of concentrated nitric and sulphuric acids, melts at 164°; 4 : 2-*nitroethylbenzoic acid*, which is produced at the same time, melts at 126°. Each acid yields an ethylic salt which boils about 290°, and in part undergoes decomposition.

5 : 2-*Amidoethylbenzoic acid* is formed on reducing the corresponding nitro-acid with tin and hydrochloric acid, and crystallises from water in colourless needles; it becomes brown on exposure to air, and melts at 179—180°. The substance is also obtained on reducing methylnitrophthalide with red phosphorus and hydriodic acid. 4 : 2-*Amidoethylbenzoic acid* also melts at 179—180°, but differs from the foregoing acid in forming a *sulphate* which is sparingly soluble.

Bis-4 : 2-*nitroethylbenzoylhydrazine*, $N_2H_2(CO\cdot C_6H_3Et\cdot NO_2)_2$, is obtained by the action of 4 : 2-nitroethylbenzoic chloride on hydrazine

hydrate; it crystallises from amylic alcohol, is sparingly soluble in ethylic alcohol, and melts, evolving gas, at 245—245·5°.

Tetrachloromethylphthalide, $CO<\substack{C_6H_4 \\ O\text{—}}>CCl\cdot CCl_3$, is obtained by submitting methylphthalide at 200° to the action of a stream of chlorine; it crystallises from 50 per cent. acetic acid, and melts at 90—91°. It is probably identical with the substance obtained from phthalylchloracetic acid by Zincke and Cooksey (Abstr., 1890, 785).

Metanitromethylphthalide, $NO_2\cdot C_6H_3<\substack{CHMe \\ CO\text{—}}>O$, produced by the action of fuming nitric acid on methylphthalide in presence of concentrated sulphuric acid, crystallises in small, yellowish needles, and melts at 104°. *Metamidomethylphthalide* is obtained by reducing the foregoing substance with phosphorus and hydriodic acid, and crystallises in long, white needles, melting at 126—127°. M. O. F.

Syntheses with Ethylic Phenylmalonate, II. By WILHELM WISLICENUS and KARL GOLDSTEIN (*Ber.*, 1896, **29**, 2599—2603. Compare Abstr., 1895, i, 368).—Ethylic phenylmalonate, when heated at 100° with alcoholic ammonia, yields a *monamide*, melting at 152°, together with, possibly, a little diamide. When heated with aniline or phenylhydrazine, it yields a *dianilide*, or a *diphenylhydrazide*, melting respectively at 201—202° and 254°, as the case may be. It will not react with methylenic or ethylenic dibromide, nor does the action of iodine on its sodium derivative result in the condensation of 2 molecules; an iodophenylmalonate appears to be formed instead.

With allylic iodide, ethylic sodio-phenylmalonate yields *ethylic phenylallylmalonate*, which boils at 176—178° under 16 mm. pressure. When this is hydrolysed, only a small quantity of *phenylallylmalonic acid* is formed; this acid melts at 145° with evolution of carbonic anhydride, and its *calcium salt* crystallises with $\frac{1}{2}H_2O$. The main product of the hydrolysis is *phenylallylacetic acid*, which melts at 34°, and boils at 260° under the ordinary pressure, at 159—160° under 25 mm.; this acid, when heated with bromine, yields no additive product, but a *monobromo*-substitution *derivative*, melting at 75°. It does not undergo molecular transformation when boiled with sodium hydroxide. C. F. B.

Tautomerism. By LUDWIG KNORR (*Annalen*, 1896, **293**, 70—120. Compare Abstr., 1894, i, 360; also Wislicenus, Abstr., 1896, i, 552, and Claisen, Abstr., 1896, i, 557).—Ethylic dibenzoylsuccinate has been hitherto obtained in three forms: (1) with an "enolic" structure, having the constitution $\begin{matrix} HO\cdot CPh\colon C\cdot COOEt \\ | \\ HO\cdot CPh\colon C\cdot COOEt \end{matrix}$, and called the α-salt, or ethylic bisphenylhydroxyacrylate; (2) the inactive ketonic form, of high melting point, prepared by von Baeyer and Perkin, and having the constitution

$$\begin{matrix} COOEt\cdot CH\cdot COPh \\ | \\ COPh\cdot CH\cdot COOEt \end{matrix} \qquad \begin{matrix} COPh\cdot CH\cdot COOEt \\ | \\ COOEt\cdot CH\cdot COPh, \end{matrix}$$

this corresponds with racemic acid, and is called the β-salt, or ethylic paradibenzoylsuccinate, and there remains (3) the inactive ketonic form of low melting point, which is known as the γ-salt, ethylic meso- or anti-dibenzoylsuccinate, and has the constitution $\begin{matrix}\mathrm{COPh{\cdot}CH{\cdot}COOEt.} \\ | \\ \mathrm{COPh{\cdot}CH{\cdot}COOEt.}\end{matrix}$ The properties of these three isomerides are in harmony with the requirements of van't Hoff's theory, the β- and γ-salts differing from one another in physical characteristics, the former being less readily fusible and soluble than the latter, whilst they behave chemically as one compound, and both yield the quinonoïd derivative, $C_{18}H_{10}O_4$ (Abstr., 1894, i, 376) when heated at 270—290°; moreover, each yields with phenylhydrazine bisdiphenylpyrazolone (*loc. cit.*), and sodium ethoxide converts both into the α-salt. The latter, on the other hand, differs in both physical and chemical properties from the β- and γ-salts. It is a liquid with strongly acid action on litmus, and dissolves readily in soda, the solid salts being neutral, whilst ferric chloride develops a dirty-brown coloration; under the influence of heat the α-salt is converted into a mixture of the β- and γ-salts.

The action of iodine on the sodium derivative of ethylic benzoylacetate yields a mixture of the β- and γ-salts, which are separated by fractional crystallisation from alcohol. When an acetic acid solution of the β-salt is heated with ammonium acetate, diethylic 2 : 5 -diphenylpyrroline-3 : 4-dicarboxylate is formed, and in the same solvent, a molecular proportion of acetic acid gives rise to bisdiphenylpyrazolone and diethylic 1-phenylamido-2 : 5-diphenylpyrroline-3 : 4-dicarboxylate, the former alone being produced in alcoholic solution. Aqueous alkalis attack the β-salt with difficulty, but in alcoholic solution it is immediately converted into the alkali derivative of the α-salt, from which carbonic anhydride liberates a mixture of the β- and γ-salts; partial conversion into the α-salt takes place when it is heated during a few minutes at 170°. The γ-salt is also transformed into the enolic form when heated at 150—160°, and with sodium ethoxide likewise yields the sodium derivative of the α-salt.

Ethylic bisphenylhydroxyacrylate, the α-salt, or enolic form of ethylic dibenzoylsuccinate, is obtained most conveniently by treating a solution of the β- or γ-salt in alcohol with an alcoholic solution of sodium ethoxide; the liquid becomes intensely yellow, and rapidly deposits the *sodium* derivative as a bright yellow, crystalline powder. It is a viscous oil, having the colour of chlorine, and after remaining 5—6 hours at the ordinary temperature has undergone partial conversion into a mixture of β- and γ-salts, a transformation which is rapidly completed at 130°. This change also occurs when the substance is dissolved in absolute or dilute alcohol, but the α-salt is stable in benzene and ethereal solutions, and in its relation to the dissociating power of solvents resembles the substances described by Wislicenus and Claisen (*loc. cit.*).

The *lactone* of hydrogen ethylic dibenzoylsuccinate,

$$\begin{matrix}\mathrm{CPh{=}C{\cdot}COOEt} \\ |\qquad\quad | \\ \mathrm{O{\cdot}CO{\cdot}C{:}CPh{\cdot}OH}\end{matrix},$$

is obtained under certain conditions which are not yet fully understood, by the partial hydrolysis of the α-salt with sodium ethoxide; it crystallises from petroleum in yellow, transparent, rhombic prisms, and melts at 64—68°. The substance is strongly acidic, develops a bluish-green colouration with ferric chloride, and when heated at 270—290° yields the quinonoïd compound, $C_{18}H_{10}O_4$; a solution of the sodium derivative has reducing properties, and in general behaviour the lactone resembles ethylic isocarbopyrotritarate (Abstr., 1894, i, 360) to which it is analogous.

Investigation of the ethylic diacetylsuccinates has yielded results which correspond with the observations recorded above; the salts occur in three isomeric forms, which are referred to as α-, β, and γ salts.

The β-salt, when heated during 5 minutes at 81°, sinters to some extent, and undergoes partial conversion into the enolic form, and when very slowly heated will melt at 87°, the melting point being 89—90° when the temperature is raised rapidly; hence the stability limit of the salt is below the melting point, whereas the ketonic forms of ethylic dibenzoylsuccinate remain stable until a temperature much higher than the melting point is reached.

Ethylic antidiacetylsuccinate (*γ-salt*), $\begin{array}{l}\mathrm{COMe{\cdot}CH{\cdot}COOEt}\\ \quad\quad\;\;\;|\\ \mathrm{COMe{\cdot}CH{\cdot}COOEt}\end{array}$, is produced along with the β-salt when the α-salt is kept at the ordinary temperature during several hours, or is heated above 60°; it melts at 68°, and the stability limit coincides with the melting point. In chemical behaviour, it resembles the β-salt, and, like that substance, is converted into the α-salt under the influence of sodium ethoxide or on application of heat.

Ethylic bishydroxycrotonate (α-salt), the enolic form of ethylic diacetylsuccinate, $\begin{array}{r}\mathrm{CH_3{\cdot}C{\cdot}OH}\\ \|\quad\;\;\\ \mathrm{COOEt{\cdot}C}\quad\;\;\\ |\quad\;\;\\ \mathrm{C{\cdot}COOEt}\\ \|\quad\;\;\\ \mathrm{OH{\cdot}C{\cdot}CH_3}\end{array}$, is obtained by the action of alcoholic sodium ethoxide on the β-salt dissolved in alcohol; it is strongly acidic, and develops an intense claret-red coloration with ferric chloride. The salt is excessively unstable, and yields a mixture of the ketonic forms if kept at the ordinary temperature, the same change being effected rapidly at 60°; in alcoholic solution it also undergoes conversion into the β- and γ-salts, remaining, however, unchanged when dissolved in ether or benzene. The conversion of the α-salt into ethylic isocarbopyrotritarate or isocarbopyrotritaric acid on hydrolysis (*loc. cit.*), the production of furfuran derivatives under the influence of concentrated acids, and the formation of ethylic dimethylpyrrolinecarboxylate by the action of ammonia, are all phenomena which accord with the configuration represented above.

The striking parallel between the author's results and those of Wislicenus and Claisen have not led him to exactly the same conclusions; whilst they, for instance, regard α-dibenzoylacetylmethane (Abstr., 1896, i, 558), a substance which is converted into the β-modification at 80—90°, as stable above 110°, because that tempe-

rature is the stability limit of the β-salt, he looks on it as a tautomeric compound, implying by this expression a mixture of isomeric substances existing above the stability limit of any single component.

[With JULIUS SCHMIDT]—Corresponding with the isomeric forms of ethylic diacetylsuccinate, the acid itself occurs in three modifications, the production of which has already been described (compare Knorr and Haber (Abstr., 1894, i, 361).

α-Diacetylsuccinic acid corresponds with the foregoing α-salt, but, owing to its unstable character, has not been obtained in the free state; its lactone, however, is the isocarbopyrotritaric acid of Knorr and Haber.

β *Diacetylsuccinic acid* arises from the γ-acid or hydrogen ethylic γ-diacetylsuccinate under the influence of concentrated sulphuric or hydrochloric acid at 170°; it crystallises from water in transparent, colourless cubes, and melts and decomposes at 185—186°.

γ-*Diacetylsuccinic acid* is the substance melting at 160° which has been hitherto described as the α-acid (*loc. cit*); the *phenylhydrazine* salt contains 2 mols. of the base, and the *silver* salt is an amorphous substance which rapidly decomposes. The *hydrogen ethylic* salt crystallises from a mixture of ether and alcohol in white, lustrous leaflets, and melts and decomposes at 150—152°.

Ethylic 2:5-*diphenylpyrroline*-3:4-*dicarboxylate*, $\begin{matrix}\mathrm{COOEt{\cdot}C{:}CPh}\\ \mid \\ \mathrm{COOEt{\cdot}C{:}CPh}\end{matrix}\!\!>\!\mathrm{NH}$,
is obtained by the action of ammonia on the ethylic salts of β-and γ-dibenzoylsuccinic acids; it crystallises from alcohol in transparent prisms, and melts at 151—152°. Phenylhydrazine converts the salts into bisdiphenylpyrazolone (Abstr., 1894, i, 376) and *ethylic* 1-anilido-2:5-diphenylpyrroline-3:4-dicarboxylate, which crystallises from glacial acetic acid in white, lustrous leaflets, and melts at 184—185°; cold, concentrated sulphuric acid forms a reddish-brown solution, which becomes deep red when heated, but this substance and the foregoing salt do not give the fir-splint reaction.

1-*Anilido*-2:5 *diphenylpyrroline*-3:4-*dicarboxylic acid*,

$$\begin{matrix}\mathrm{COOH{\cdot}C{:}CPh}\\ \mid \\ \mathrm{COOH{\cdot}C{:}CPh}\end{matrix}\!\!>\!\mathrm{N{\cdot}NHPh},$$

is obtained on hydrolysis, and separates from dilute alcohol in small, white crystals containing $1H_2O$, which melt and vigorously decompose at 154°; it does not give the fir-splint reaction, and when heated liberates carbonic anhydride, forming a sublimate of yellowish red crystals, most probably consisting of anilidodiphenylpyrroline.

The double anhydride of dibenzoylsuccinic acid, $C_{18}H_{10}O_4$, is the quinonoïd substance, described by Knorr and Scheidt, obtained on heating the ethylic β- and γ-salts; when heated with concentrated aqueous ammonia at 100°, it yields the *compound* $C_{18}H_{13}NO_4$, which crystallises from alcohol in yellow, rhombic prisms, and melts and decomposes at 202—203°. When the gas generated by nitric acid and arsenious anhydride is passed into a solution of the quinone in acetic

acid, the *compound* $C_{18}H_{10}O_4,2HNO_3$ is produced, and separates in white, transparent prisms, containing $1\frac{1}{2}$ mol. of the solvent; at 60°, this substance evolves oxides of nitrogen, and acetic acid, the residue consisting of the original quinone. The same additive compound is formed when the action proceeds in ethereal solution, but after further treatment with the gas, effervescence occurs, and rapidly becomes vigorous; as this ceases, benzoylpyruvic acid separates in yellowish-white prisms, melting at 159—161°.

The *anhydride* of hydrogen ethylic dibenzoylsuccinate, $C_{22}H_{16}O_5$, constitutes the intermediate product in the formation of the quinone and crystallises from amylic alcohol in yellowish-white rhombohedra, which darken at 190°, and melt at 198—200°, evolving gas; it dissolves sparingly in the usual solvents, and exhibits green fluorescence. The substance is insoluble in cold alkalis, but dissolves slowly when heated; it forms a deep, purple-red solution with concentrated sulphuric acid, and is converted into the quinone if heated to 280°.

M. O. F.

Action of Alkali on Benzsulphydroxamic Acid [Benzenesulphonylhydroxylamide]. By EDWARD DIVERS (*Ber.*, 1896, **29**, 2324. Compare Piloty, Abstr., 1896, i, 555).—A claim for priority in a method for the preparation of hyponitrites. (Compare Trans., 1889, 767).

J. F. T.

Action of Acid Amides on Benzoin. By ALFRED NEWLIN SEAL. (*J. Amer. Chem. Soc.*, 1896, **18**, 101—119).—The author has heated alcoholic solutions of various acid amides with benzoin in sealed tubes, and finds that the amide is in all cases decomposed by the alcohol, yielding the ethylic salt of the corresponding acid and ammonia, the latter then reacts with the benzoin, yielding tetraphenylazine, $C_4N_2Ph_4$; benzoinam, $C_{28}H_{24}N_2O$; benzoinidam, $C_{28}H_{23}NO_2$, and lophine, $C_3N_2HPh_3$. Compare Japp and Wilson, Japp and Burton, (Trans., 1886, **49**, 825, 843; 1887, **51**, 98). Similar results were obtained on heating the amides with benzoin in the absence of alcohol.

All attempts to prepare bromo- and chloro-derivatives of tetraphenylazine proved unsuccessful. Braun and Meyer's tetranitrotetraphenylazine (*Ber.*, 1888, **21**, 1269), when reduced with tin and hydrochloric acid, yields a yellow, amorphous *tetramido*-derivative which darkens when heated, and melts above 260°, at the same time undergoing decomposition. Its *hydrochloride* does not crystallise, but on evaporation of its aqueous solution in a vacuum, it is deposited as a reddish-brown, transparent mass. It melts at about 140° and is readily soluble in water. The *platinochloride*,

$$C_4N_2(C_6H_4NH_2HCl)_4,PtCl_4 + 11H_2O,$$

forms a reddish-brown precipitate. The crystallographic properties of tetraphenylazine are given in detail.

Carbamide and benzoin, when heated together with alcohol at 175—195°, yield diphenylacetylenureïn, $\begin{matrix}CPh\cdot NH\\ | \\ CPh\cdot NH\end{matrix}\!\!>\!CO$. (Compare Abstr., 1895, i, 304.)

J. J. S.

The Aluminium Chloride Reaction. By MORIZ FREUND (*Monatsh.*, 1896, 395—400).—In preparing orthonitrodiphenylmethane by the action of aluminium chloride on a mixture of orthonitrobenzylic chloride and benzene, a resinous bye-product is obtained in which occur the hydrochlorides of two bases; a vigorous action appears to be conducive to their production. One of these is present in small quantity, and crystallises in colourless needles; it yields a *base*, also in the form of colourless needles, melting at 185—190°.

The second *substance* crystallises in yellow needles and is decomposed by boiling water, with production of the free *base* $C_{13}H_9NO$. This separates from dilute alcohol in beautiful, bright-yellow, glistening needles, and melts at 169°; it does not give the reactions characteristic of primary amines. When subjected to the action of nitrous acid, the base yields a yellow *compound* which does not melt below 350° and dissolves in dilute potash, giving a dark red solution similar to that produced by the oxyfluorenone of Graebe and Schestakow. (Compare Abstr., 1895, i, 372); when reduced in ethereal solution by means of zinc, the yellow compound yields a substance which, after distillation and crystallisation from dilute alcohol, melts at 168—172° and gives a reddish-brown precipitate when its aqueous solution is mixed with one of picric acid. The above base is not identical with acridone, phenanthridone or orthoamidofluorenone which have the same composition.

When a mixture of benzene and nitrobenzene is heated with aluminium chloride on the water bath Heusler's paramidodiphenyl was obtained; the yield was 8·5 per cent. of the weight of nitrobenzene employed. A. L.

Ditolylimide. By HERMANN SEYBERTH (*Ber.*, 1896, **29**, 2594).—This substance, $\begin{matrix} C_6H_3Me \\ | \\ C_6H_3Me \end{matrix}\!\!>NH$, is formed to some extent when orthotoluidine vapour is passed through a heated glass tube packed with fragments of pumice. It forms crystals with a yellowish-green surface lustre, and its solution in hot alcohol has a greenish fluorescence; it melts at 364° (uncorr.), and exhibits many of the reactions of carbazole. C. F. B.

Formation of Desylacetic Acid from Phenylpyruvic Acid and Benzaldehyde. By EMIL ERLENMEYER, jun. (*Ber.*, 1896, **29**, 2585—2588).—The oxylactone $CHPh<\begin{matrix} CHPh\cdot O \\ \quad\quad | \\ CO——CO \end{matrix}$ (Abstr., 1894, i, 592), when reduced by boiling with zinc dust and acetic acid, yields the zinc salt of an unsaturated acetylmonhydroxy-acid, which, when boiled with hydrochloric acid, yields desylacetic acid,

$$\rightarrow OAc\cdot CHPh\cdot CHPh\cdot CH(OH)\cdot COOH \rightarrow OAc\cdot CPh{:}CPh\cdot CH_2\cdot COOH$$
$$\rightarrow OH\cdot CPh{:}CPh\cdot CH_2\cdot COOH \qquad \rightarrow COPh\cdot CHPh\cdot CH_2\cdot COOH$$

Desylacetic acid really crystallises in tetragonal octahedra ($a : c = 1 : 0\cdot9374$), although the crystals have the appearance of regular octahedra. C. F. B.

Phthaleïn Derivatives. By JOSEF HERZIG and HANS MEYER (*Monatsh.*, 1896, **17**, 429—441).—Dimethylphenolphthaleïn, prepared by the action of methylic iodide on a solution of phenolphthaleïn in absolute alcohol, forms white, shining leaflets, and melts at 97—99°; it is insoluble in dilute alkalis, but is attacked by boiling, strong alcoholic potash, and the product, after separation from alcohol, is readily soluble in water, but yields the original compound on the addition of acids. This behaviour is not in accordance with the supposition that the substance is a lactonic salt. The compound cannot be benzoylated, and is precipitated from its solution in sulphuric acid on adding water; it is reduced, however, by zinc in alkaline solution, and the product melts at 144—146°, and has all the characteristics of a dimethoxytripheny methanecarboxylic acid (compare Baeyer, Abstr., 1880, 650, and 1896, i, 564).

The authors have not succeeded in preparing lactonic diethoxyfluoresceïn; the monethoxy-compound, however, they find to act as a quinonoïd compound on etherification, and as a lactone on bromination, no compound resembling eosin being produced in the latter instance.

Monethylic fluoresceïncarboxylate yields a quinonoïd *acetyl* derivative, $C_{20}H_{10}O_5EtAc$, which crystallises in yellow needles, melting at 189—190°.

As the authors have already pointed out (Abstr., 1896, i, 237), the formation of an amido-compound on reducing the oxime of phenolphthaleïn militates against Friedländer's formula for the latter substance; they have repeated his experiments and confirmed his results. The product of reduction, $C_{20}H_{17}NO_3 + EtOH$, melts at 253—257°, dissolves in potash, is precipitated by carbonic anhydride, and yields a *diacetyl* derivative, $C_{20}H_{15}NO_3Ac_2$, which crystallises from alcohol in white needles melting at 205—208°; this substance is not identical with Errara and Gasparini's phenolphthalimide (Abstr., 1894, 294), but this fact does not exclude the possibility of it being an isomeride. Errari and Gasparini assign to their substance the structure $C_6H_4{<}{\scriptstyle C(C_6H_4\cdot OH)_2 \atop \scriptstyle CO\text{———}}{>}NH$; it is more probable, however, that this represents the constitution of Friedländer's compound, and that the other has the asymmetric formula $C_6H_4{<}{\scriptstyle C(C_6H_4\cdot OH)_2 \atop \scriptstyle C(NH)\text{——}}{>}O$; the first formula has the advantage that it explains the observation, made by Friedländer, that the "oxime" suffers decomposition into parahydroxyorthobenzoylbenzoic acid and paramidophenol.

The authors advance further reasons for discarding the old "oxime" formula, and point out that a substance having the constitution $COOH\cdot C_6H_4\cdot C(C_6H_4\cdot OH)\colon C_6H_4\colon NOH$ should yield either a monacetyl or a diacetyl compound, soluble in alkali; the compound in question, however, yields at least three substances on acetylation, none of which are soluble in alkalis. A. L.

The Phthaleïn-group. II. Fluoresceïn. By RICHARD E. MEYER and HEINRICH MEYER (*Ber.*, 1896, **29**, 2623—2626).—Baeyer has shown (this Journal, 1877, i, 195) that dihydroxybenzoylbenzoic acid,

when heated at its melting point, yields phthalic anhydride and fluoresceïn. The authors find that a similar change takes place when dibromodihydroxybenzoylbenzoic acid is heated at 230—240°, phthalic anhydride and eosin being produced; the change is most readily effected when 20 per cent. of zinc chloride is introduced and the operation conducted in a stream of hydrogen.

The production of eosin from dibromodihydroxybenzoylbenzoic acid in the manner described above makes it appear certain that the former substance has the symmetrical structure:

$$O<{C_6HBr_2(OH) \atop C_6HBr_2(OH)}>C<{C_6H_4 \atop -O-}>CO$$

[$O:Br_2:OH:C = 6:5:3:4:1$ in each ring.]

The product obtained on melting dibromodihydroxybenzoylbenzoic acid contains a considerable proportion (about 56 per cent.) of a red substance, which, on reduction and reoxidation, yields fluoresceïn.

A. L.

The Phthaleïn-group. III. Orcinolphthaleïns. By RICHARD E. MEYER and HEINRICH MEYER (*Ber.*, 1896, **29**, 2627—2640).—The crude product obtained by heating orcinol with phthalic anhydride in presence of a condensing agent (compare Fischer, this Journal, 1877, i, 205) consists of three substances of the phthaleïn type, to which the authors refer as α-, β-, and γ-orcinolphthaleïn respectively.

α-Orcinolphthaleïn is obtained from the mixture by extraction with cold dilute alkalis, which leave it undissolved; it separates from acetic acid in colourless crystals. It dissolves in strong alkalis with production of a bluish-red coloration, but is only sparingly soluble in dilute soda and ammonia; its properties are those of a very weak acid, but it is extracted from its alkaline solution by means of ether. On adding alcoholic potash to an alcoholic solution of the phthaleïn, the *potassium* salt separates in the form of blue needles, having a bronze-like lustre. α-Orcinolphthaleïn yields the additive compound with hydrogen chloride described by Fischer (*loc. cit.*), but could not be made to form the monacetyl derivative obtained by him; the latter is doubtless the compound, described later, obtained from β-orcinolphthaleïn. The *dibenzoyl* derivative, $C_{22}H_{14}O_5Bz_2$, which is formed on shaking the alkaline solution of the phthaleïn with benzoic chloride, is not dissolved by cold alkali, but is slowly hydrolysed by hot alcoholic potash; it dissolves readily in chloroform, and hot benzene, is sparingly soluble in methylic alcohol, ethylic alcohol and acetone, but is insoluble in light petroleum; it crystallises from alcohol, on the addition of benzene, in the form of colourless crystals melting at 284—285°.

Tetrabrom-α-orcinolphthaleïn, $C_{22}H_{12}Br_4O_5$, is formed on adding bromine to a solution of α-orcinolphthaleïn in glacial acetic acid; it crystallises from hot nitrobenzene in yellowish prisms, and dissolves in aqueous soda, the resulting solution having a violet colour which is changed to an intense blue by heat.

α-Orcinolphthaleïn is easily reduced in alkaline solution by means of zinc dust, the corresponding *α-orcinolphthalin*, $C_{22}H_{18}O_5$, being produced. The latter forms thick quadratic crystals, which fall to

pieces at 130°, water being eliminated; it melts with effervescence at 256°, reversion to the corresponding phthaleïn occurring simultaneously; the latter change is most readily effected when the hot alkaline solution of the phthalin is oxidised with potassium ferricyanide. An *acetyl* compound, $C_{24}H_{18}O_5$, is obtained when the foregoing phthalin is heated with acetic anhydride; it separates from alcohol in thick rhombohedra, melting at 219°, is insoluble in alkalis but is gradually hydrolysed when boiled with them.

β-Orcinolphthaleïn, $C_{22}H_{16}O_5 + \frac{1}{2}H_2O$, constitutes the portion of the above crude product which is soluble in ammonia but is precipitated from this solution on exposure to the atmosphere. It crystallises in microscopic bundles of needles or large, six-sided, orange tables. The properties and analyses of the substance are in agreement with those of the "monacetylorcinolphthaleïn" described by Fischer, and the two substances are doubtless identical. It dissolves readily in ethylic and methylic alcohols and ethylic acetate, yielding brown solutions, and is sparingly soluble in hot water, benzene, and acetic acid. Aqueous solutions of alkalis, alkali carbonates or ammonia dissolve it, and yield solutions of a cherry-red colour, which is not destroyed by dilution; the addition of acid, however, causes the reprecipitation of the phthaleïn. Hydrochloric acid combines directly with the substance with production of a compound similar to that obtained from the α-phthaleïn. It is reduced by soda and zinc dust to the corresponding *phthalin,* which dissolves sparingly in hot benzene, and separates in crystals on cooling; on cautious oxidation, it is reconverted into the original phthaleïn.

Diacetyl-β-orcinolphthaleïn, $C_{22}H_{14}O_5Ac_2$, forms bundles of yellow needles, melting at 227—228°. *Dibenzoyl-β-orcinolphthaleïn,*

$$C_{22}H_{14}O_5Bz_2,$$

forms colourless, shining crystals, and melts at 244—245°.

Tetrabromo-β-orcinolphthaleïn, $C_{22}H_{12}Br_4O_5$, crystallises in colourless shining tables; it dissolves in alkali carbonates with production of a greenish-black solution, which, on dilution, becomes a dirty red. This is doubtless the tetrabromorcinolphthaleïn actually isolated by Fischer, as its properties are in complete accordance with those of that substance. It is reduced to the β-phthalin by zinc dust and caustic potash.

γ-Orcinolphthaleïn, $C_{22}H_{16}O_5$ is obtained from the crude mixture of phthaleïns by the action of gaseous ammonia, followed by dissolution in water; the solution, on exposure to the atmosphere, deposits the β-phthaleïn, the filtered liquid yielding the γ-compound when acidified with sulphuric acid. When its ammoniacal solution is mixed with alcohol and sulphuric acid, and then evaporated, the substance separates in pale yellow prisms, whilst a concentrated solution in acetic acid deposits dark orange crystals.

γ-Orcinolphthaleïn dissolves in alcohol, forming a brown solution, from which it is deposited in bundles of bright yellow, short needles. It bears a strong resemblance to fluoresceïn; when precipitated in the amorphous state it is yellow, whilst its solutions in ammonia, alkalis, or their carbonates are brown, and show a greenish fluor-

escence weaker than that of fluoresceïn; it acts as a dye, imparting a yellowish hue to silk. It dissolves in warm sodium acetate or phosphate, forming solutions which exhibit a fluorescence not affected on extracting the liquids with ether; it is also somewhat soluble in hydrochloric and dilute sulphuric acids. Its solution in ether is not fluorescent. It is reduced by zinc-dust and soda, with production of the colourless phthalin, which readily suffers reoxidation on treatment with potassium permanganate.

Diacetyl-γ-orcinolphthaleïn, $C_{22}H_{12}O_5Ac_2$, melts at 207—208°, and crystallises in colourless prisms.

Tetrabromo-γ-orcinolphthaleïn, $C_{22}H_{14}Br_4O_5$, crystallises in flat, truncated, brownish prisms. It is very sparingly soluble in all the ordinary media; it dissolves in alkalis and alkali carbonates, forming intense eosin-red solutions without fluorescence, but which are yellowish-red by reflected, and a rose-colour by transmitted light. Gaseous ammonia imparts a rose colour to the compound, which is finally transformed into the ammonium salt, a substance having a green metallic lustre; it dyes silk a beautiful eosin-red. When it is heated with sodium hydroxide, a deep blue solution is obtained, which contains two substances, one soluble in water and having an odour reminiscent of bromophenol, the other insoluble in water and precipitated by acids. It is completely reduced in alkaline solution with sodium amalgam, the phthalin thus formed being very readily oxidised to a coloured, fluorescent substance.

The three foregoing orcinolphthaleïns are doubtless constituted in the manner indicated by the formulæ,

$$\overset{6}{O}<\begin{matrix}C_6H_2\overset{4}{Me}(\overset{2}{OH})\\ C_6H_2\underset{4}{Me}(\underset{2}{OH})\end{matrix}>\overset{1}{C}<\begin{matrix}C_6H_4\\ -O-\end{matrix}>CO, \qquad O<\begin{matrix}C_6H_2\overset{4}{Me}(\overset{2}{OH})\\ C_6H_2\underset{2}{Me}(\underset{4}{OH})\end{matrix}>C<\begin{matrix}C_6H_4\\ -O-\end{matrix}>CO,$$

I II

$$O<\begin{matrix}C_6H_2\overset{2}{Me}(\overset{4}{OH})\\ C_6H_2\underset{2}{Me}(\underset{4}{OH})\end{matrix}>C<\begin{matrix}C_6H_4\\ -O-\end{matrix}>CO.$$

III

Of these formulæ, III undoubtedly represents the fluorescent γ-orcinolphthaleïn. A. L.

Patent-blue Colouring Matters; derivatives of Benzylsultone, Benzylsultame, and Benzylidenesultime. By PAUL FRITSCH (*Ber.*, 1896, **29**, 2290—2301).—"*Pseudosaccharin*" *chloride*, $C_6H_4<\begin{matrix}CCl\\ SO_2\end{matrix}>N$, was obtained by Jesurun (Abstr., 1893, i, 716) in crystals which melt at 143—145°; repeated crystallisation from benzene has raised the melting point to 149°.

Phenylbenzylidenesultime, $C_6H_4<\begin{matrix}CPh\\ SO_2\end{matrix}>N$, is the substance obtained by Remsen and Saunders on treating orthobenzoylbenzenesulphonic chloride with ammonia (Abstr., 1895, i, 475); the author has prepared it by heating the foregoing chloride with benzene and aluminium chloride, and it crystallises in lustrous, rhombic plates,

melting at 164°. The same action gives rise to *diphenylbenzylsultame*, $C_6H_4<{CPh_2 \atop SO_2}>NH$, which crystallises in prisms, and melts at 210°; the *potassium* derivative crystallises in long, colourless needles.

Dimethylparamidophenylbenzylidenesultime,

$$C_6H_4<{C(C_6H_4\cdot NMe_2) \atop \text{———}SO_2\text{———}}>N,$$

is produced when "pseudosaccharin" chloride is heated with dimethylaniline and aluminium chloride; it crystallises from toluene in colourless leaflets, and melts at 221°.

The author confirms the views of Remsen and Saunders (*loc. cit.*) regarding the isomeric chlorides of orthosulphobenzoic acid, and the paper also contains a description of the preparation of tetramethylparatriamidotriphenylmethaneorthosulphonic acid from tetramethyldiamidobenzhydrol and metamidobenzenesulphonic acid. M. O. F.

Triphenylethanone [Diphenylacetophenone]. By A. COLLET (*Bull. Soc. Chim.*, 1896, [3], **15**, 22—23).—Trichloracetic chloride, when heated with benzene, gives diphenylacetophenone, $CHPh_2\cdot COPh$ (Delacre, Abstr., 1896, i, 485), whilst chloracetic chloride, under similar conditions, gives phenylacetophenone (phenyl benzyl ketone). It was therefore of interest to ascertain what the dichlor-acid would give. A mixture of dichloracetic chloride, benzene, and aluminium chloride, when heated for 10 hours on a water bath, yields diphenylacetophenone. M. W. T.

Dyes of the Pyronine Group. By JOACHIM BIEHRINGER (*J. pr. Chem.*, 1896 [2], **54**, 217—258. Compare Abstr., 1895, i, 146).—Metadiethylamidophenol melts at 78°, not at 74° (*loc. cit.*); its *hydrochloride*, $C_{10}H_{15}NO,HCl + \frac{1}{2}H_2O$, was prepared. Tetramethyldiamidodihydroxydiphenylmethane melts at 178°, not at 175° (Abstr., 1895, i, 47); the hydrochloride of its benzoyl derivative, $C_{17}H_{20}N_2O_2Bz_2,2HCl$, melts at 72—73°, not at 141° (Abstr., 1895, i, 147).

Tetraethyldiamidodihydroxydiphenylmethane, $CH_2[C_6H_3(OH)\cdot NEt_2]_2$, is prepared by dissolving metadiethylamidophenol (11 grams) in wood spirit (25 c.c.), adding fuming hydrochloric acid (3 c.c.), cooling and mixing with formaldehyde (2·5 c.c. of a 40 per cent. solution); after a time, crystallised sodium acetate (4·5 grams) dissolved in twice its weight of wood spirit is added, and the solution is slowly evaporated. It crystallises in prisms, melts at 168°, and dissolves in hot alcohol and xylene, but only sparingly in hot acetone.

The *sulphate*, $C_{21}H_{30}N_2O_2,H_2SO_4$, was prepared. Details of the production of tetramethyldiamidodiphenylmethane oxide (*loc. cit.*) by the action of sulphuric acid on the dihydroxy-base are given, together with prescriptions for oxidising the oxide to the colouring matter, known as pyronine, both by chloranil and by sodium nitrite. Pyronine *dihydrochloride*, $C_{17}H_{20}N_2OCl_2 + H_2O$, crystallises in flat prisms with a blue lustre when the pyronine is dissolved in 20 per

cent. hydrochloric acid and the solution is evaporated; when dried in a xylene bath, until constant in weight, it passes into the green *hydrochloride*, $C_{17}H_{21}N_2OCl + \frac{1}{2}H_2O(?)$. The *platinochloride*,

$$(C_{17}H_{20}N_2O)_2,H_2PtCl_6,$$

crystallises in prisms with a green lustre.

Tetramethyldiamidoxanthone, $CO{:}[C_6H_3(NMe_2)]_2{:}O$, is the compound previously mentioned (*loc. cit*) as obtainable from the anhydro-base by the prolonged action of sulphuric acid. It is an oxidation product, and is formed in small quantity in most of the reactions of the group of dyes under consideration; thus, treatment of pyronine with potassium ferricyanide in alkaline solution yields a crude mass from which the xanthone may be extracted by appropriate solvents to the extent of about 10 per cent. of the pyronine. It crystallises from alcohol in yellowish prisms with oblique ends, or in aggregates of needles, melts at 240—242°, and dissolves in hot wood spirit, alcohol, acetone, chloroform, ethylic acetate, carbon bisulphide and benzene, "sparingly in hot ligroin and hardly at all in petroleum-benzin." The solutions in the first three of these solvents and also that in strong sulphuric acid show a blue fluorescence; this fact, together with the yellow colour of the crystals, leads to the conclusion that the compound is a xanthone derivative. The blue fluorescence passes to green in dilute acid solutions. The *hydrochloride*, $C_{17}H_{18}N_2O_2,HCl$, and the *platinochloride* are described, also a *tribromo*-derivative, $C_{17}H_{15}Br_3N_2O_2$, obtained by direct bromination in a glacial acetic acid solution.

To prove the constitution of pyronine, tetramethyldiamidodiphenylmethane was nitrated to the dinitro-derivative of melting point 190—191° (Abstr., 1895, i, 98), this was reduced to the tetramido-compound (*loc. cit.*), the orientation of which was diagnosed by the fact that when heated in a sealed tube at 140° with hydrochloric acid and subsequently oxidised by air or ferric chloride, it yields *tetramethyldiamidoacridine*, $CH{<}^{C_6H_3(NMe_2)}_{C_6H_3(NMe_2)}{>}N$ (see below). The formation of this compound shows that there are two amido-groups in tetramethyltetramidodiphenylmethane which are both in the ortho-position relatively to the methylene group. This orientation having been settled, it only remained to convert the tetramido-compound into the dihydroxy-derivative by means of the diazo-reaction; the compound thus produced $[CH_2:OH:NMe_2 = 1:2:4]$, was proved to be identical with the condensation product of formaldehyde and dimethylmetamidophenol. It follows from this that the oxygen in the anhydro-base formed by oxidising the dihydroxy-derivative joins two ortho-positions in the two benzene nuclei, and that the colour base of pyronine is a carbinol of the form $OH{\cdot}CH{<}^{C_6H_3(NMe_2)}_{C_6H_3(NMe_2)}{>}O$, which passes into the dye $CH{<}^{C_6H_3{-}(NMe_2)}_{C_6H_3({:}NMe_2Cl)}{>}O$. The formation of the xanthone from the carbinol is self-evident.

Tetramethyldiamidoacridine (see above) crystallises in yellow needles, melts at 181—182°, and dissolves in water, alcohol, acetone, and

hot benzene; in strong sulphuric acid it gives a yellow solution with a blue fluorescence. The *hydrochloride* and *platinochloride* are described.

The condensation of benzaldehyde with metadimethylamidophenol, producing rosamine, is discussed. The compound primarily formed is an orthodihydroxyleuco-malachite green (m. p. 176°), which readily undergoes intramolecular dehydration, yielding an anhydride of the pyronine class, capable of similar oxidation to a dye, which, however, is a sulphonic salt. A. G. B.

Ketones derived from Naphthalene. By L. ROUSSET (*Bull. Soc. Chim.* [3], 15, 58—72).—By the addition of an equivalent of an acid chloride in small quantities to a boiling solution of naphthalene in carbon bisulphide with aluminium chloride, the author obtains a fair yield of a mixture of the α- and β-substituted naphthalenes of the formula $R{\cdot}CO{\cdot}C_{10}H_7$. In some cases, the two isomerides can be separated by direct crystallisation, but it is, as a rule, more advantageous to first obtain the compounds which the ketones form with picric acid, $R{\cdot}CO{\cdot}C_{10}H_7,C_6H_2(NO_2)_3{\cdot}OH$, which differ more widely in their solubilities in alcohol than the ketones themselves. These picrates are easily decomposed by means of sodium carbonate into sodium picrate and the ketone. The α- and β-ketones yield α- and β-naphthoic acids on oxidation with nitric acid.

α-Naphthyl methyl ketone, an almost colourless liquid, has a sp. gr. = 1·1336 at 0°, boils at 295—296°, and is soluble in organic solvents. Its oxime melts at 135—136°, and its picrate melts at 116°, and is very insoluble in alcohol.

β-Naphthyl methyl ketone forms white needles; melts at 51°, boils at 171—172° under 11 mm. pressure, and is not very soluble in alcohol and light petroleum, Its *oxime* melts at 142—143°, and its *picrate* is very soluble in alcohol.

α-Naphthyl ethyl ketone is a liquid boiling at 166—168° under 8 mm. pressure; it is insoluble in water and only slightly soluble in cold light petroleum, soluble in chloroform, alcohol, &c. The *oxime* is crystalline, and melts at 57—58°; the *picrate* melts at 77—78°, and is very insoluble in alcohol.

β-Naphthyl ethyl ketone is a crystalline substance melting at 56—57°, and boiling under atmospheric pressure at 312—314°; it is slightly soluble in cold, light petroleum or alcohol. The *oxime* melts at 133°.

α-Naphthyl propyl ketone is a liquid of sp. gr. = 1·0861 at 0°; it boils under atmospheric pressure at 316—318°, and is soluble in organic solvents. The *oxime* is a liquid, boiling at 206—208° under 13 mm. pressure. The *picrate* is soluble in alcohol.

β-Naphthyl propyl ketone, a solid very difficult to free from alcohol, melts at 50—51°, boils at 322—324°, and is soluble in alcohol. The *oxime* melts at 89°. The *picrate* is almost insoluble in alcohol.

α-Naphthyl isopropyl ketone is a liquid of sp. gr. = 1·0761 at 0° which boils at 308—310° under atmospheric pressure, and is soluble in organic solvents. The *oxime* is a solid, melting at 140°, or after fusion at 125°. The *picrate* melts at 66—67°, and is very insoluble in alcohol.

β-Naphthyl isopropyl ketone, a liquid of sp. gr. = 1·0617 at 0°; it boils at 312—314°, and is soluble in organic solvents. The *oxime* melts at 121—122° and boils at 200—203° under 12 mm. pressure.

a-Naphthyl isobutyl ketone, a liquid of sp. gr. = 1·059 at 0°, boils at 319—321° under atmospheric pressure, and at 180—182° at 9 mm. pressure. The *oxime* is a viscous liquid, boiling at 200—205° at 10 mm. pressure. The *picrate* is soluble in alcohol.

β-Naphthyl isobutyl ketone, a liquid of sp. gr. = 1·050 at 0°; boils at 323—325°, and is soluble in organic solvents. The *oxime* melts at 99°, and boils at 208—210° at 10 mm. pressure. The *picrate* is only slightly soluble in alcohol.

The naphthyl phenyl ketones are easily separated by treating the mixture of picrates with benzene, in which the β-derivative is very insoluble; it melts at 82°, and its picrate melts at 112—113.°

M. W. T.

β-Naphthylacetic Acid. By OSCAR BLANK (*Ber.*, 1896, **29**, 2373—2375.)—*β-Naphthylacetonitrile*, $C_{10}H_7·CH_2·CN$, may be prepared in the usual way from the corresponding chloride, and crystallises in white, spherical masses, melting at 79—81°. *β-Naphthylacetic acid* separates from hot water in irregular, nacreous crystals, melting at 137·5—139°. The *silver* salt crystallises in lustrous plates, and the *methylic* salt is a thick, light yellow oil. The acid is converted into an ethereal salt when it is simply heated with an alcohol. When distilled, it decomposes into β-methylnaphthalene and carbonic anhydride. It reacts with phthalic anhydride and sodium acetate to form *β-naphthylmethylenephthalide*, $CO<{-O-\atop C_6H_4}>C:CHC_{10}H_7$, which crystallises in golden yellow needles, melting at 170—171°.

A. H.

Action of Nitric Acid on Bromoprotocatechuic Acid; Conversion into 3 : 4′-Dibromo-β-naphthaquinone-2′-carboxylic Acid. By E. C. THEODOR ZINCKE, BRUNO FRANCKE [and in part, MAX SCHMIDT], (*Annalen*, 1896, **293**, 120—175. Compare Abstr., 1896, i, 308).—3 : *4′-Dibromo-β-naphthaquinone-2′-carboxylic acid*, obtained by the cautious oxidation of bromoprotocatechuic acid in small quantities by dilute nitric acid, crystallises from glacial acetic acid in dark red needles, which melt at 253—254°, and contain 1 mol. of the solvent; it is very readily soluble in acetone, less easily in alcohol and hot glacial acetic acid, and only sparingly in ether, chloroform and benzene. The *sodium* salt is sparingly soluble, and the red colour of the solution slowly changes to brownish green.

3 : *4′-Dibromo-β-naphthaquinol-2′-carboxylic acid* is formed when the quinone is reduced with stannous chloride in acetic acid, and crystallises from hot acetic acid in yellowish aggregates; concentrated nitric acid regenerates the quinone, and both chlorine and caustic soda convert the quinol into the same compounds as its oxidation product. The *diacetyl* derivative crystallises from glacial acetic acid in colourless leaflets, and melts at 239°.

Dibromonaphthazinecarboxylic acid, $C_6H_4<\overset{N}{\underset{N}{|}}>C_{10}H_3Br_2\cdot COOH$, is obtained by the action of orthophenylenediamine on dibromonaphthaquinonecarboxylic acid dissolved in glacial acetic acid; it dissolves sparingly in the usual solvents, and forms an intense yellow solution in concentrated nitric acid, whilst concentrated sulphuric acid develops a dark violet coloration.

3:4':2-*Dibromhydroxy-α-naphthaquinone-2'-carboxylic acid* is produced by treating the quinone or quinol with dilute caustic soda, the lactone of 4-α-bromo-β-hydroxypropionyl-5-bromisophthalic acid (see below) being formed at the same time; it separates from glacial acetic acid in small needles containing 1 mol. of the solvent, and decomposes evolving gas at 281°. The *sodium* and *ammonium* salts are dark ·d, and sparingly soluble; the *eurhodole*, obtained from orthophenylenediamine, crystallises in slender, red needles, and forms sparingly soluble, red, alkali salts. Oxidation of the acid with potassium permanganate gives rise to bromomellithic acid, and chlorine converts it into chlorodibromo- and dichlorobromo-triketonaphthalenecarboxylic acid, according to the conditions observed.

3:3:4'-*Dichlorobromo*-1:2:4-*triketohydronaphthalene-2'-carboxylic acid*, $\begin{array}{l}COOH\cdot C{:}CH—\cdot C\cdot CO\cdot CO\\ \quad\ \ | \qquad\quad\ \ \| \qquad\ \ |\\ \quad CH{:}CBr\cdot C\cdot CO\cdot CCl_2\end{array}$, H_2O, is obtained by suspending chlorobromohydroxynaphthaquinonecarboxylic acid in chloroform, and passing chlorine into the liquid; it contains 1 mol. H_2O, even after recrystallisation from a mixture of ether and light petroleum, separating in colourless needles, which char and evolve gas at 200°. Stannous chloride converts the triketo-compound into 3:4:2-chlorobromhydroxy-α-naphthaquinonecarboxylic acid, the substance from which it was obtained; this acid will be described subsequently.

2':2':4-*Dichlorobromo-1'-hydroxy-3'-ketohydrindene-2:1'-dicarboxylic acid*, $COOH\cdot C_6H_2Br<\begin{array}{c}C(OH)(COOH)\\ \hline CO\end{array}>CCl_2$, is produced with great readiness when water acts on the foregoing acid, and is obtained by acidifying an alkaline solution of that substance; it crystallises from hydrochloric acid in four-sided plates containing $3H_2O$, which is removed at 100°, and the anhydrous substance chars and liberates gas at 215°. When crystallised from nitric acid of sp. gr. = 1·4, it contains $1H_2O$, and melts with vigorous effervescence at 160°, subsequently charring at 200°. The aqueous solution gradually becomes red, and yields an amorphous, red precipitate, owing to elimination of hydrogen chloride; in consequence of this change, which proceeds rapidly with boiling water, it is necessary to crystallise the substance from mineral acids. The *dimethylic* salt crystallises from benzene, and melts at 168—169°; it dissolves at once in caustic soda, and develops a red coloration. The acid is indifferent towards boiling, concentrated nitric acid, but is oxidised by chromic acid to the corresponding keto-compound, and finally yields bromotrimellithic acid.

2':2':4-*Dichlorobromo*-1':3'-*diketohydrindene-2-carboxylic acid*,

$$COOH\cdot C_6H_2Br<\begin{array}{c}CO\\CO\end{array}>CCl_2,$$

is obtained by the action of aqueous chromic acid solution on the foregoing compound, and is almost insoluble in ether, light petroleum, benzene, and concentrated hydrochloric and nitric acids; it crystallises from alcohol, and becomes red and effervesces at 280°. Sodium carbonate dissolves the substance with development of a red colour, and hydrochloric acid precipitates from the solution *4-dichloraceto-5-bromisophthalic acid*, which crystallises from nitric acid of sp. gr. = 1·4, and melts evolving gas at 226—227°; alkalis eliminate chlorine from the substance, which is indifferent towards oxidising agents. *4-Trichloraceto-5-bromisophthalic acid* is obtained by digesting the indene derivative with a solution of bleaching powder, and after some hours acidifying the liquid with hydrochloric acid; it dissolves with difficulty in water, dilute acids, benzene, and chloroform, and crystallises from nitric acid in small octahedra, sintering at 220°, and melting at 235°. The *dimethylic* salt is crystalline and melts at 169°.

5-Bromotrimellithic acid may be obtained from any of the foregoing substances by the action of potassium permanganate or chromic acid, chlorobromo- or dibromo-hydroxynaphthaquinonecarboxylic acid being the most convenient source; it separates from nitric acid of sp. gr. = 1·4 in minute crystals, and melts at 237°. The *dimethylic* salt crystallises from water in long, slender needles, and melts at 130—131°; the *trimethylic* salt crystallises from methylic alcohol in aggregates of small needles, and melts at 110°.

3:3:4′-*Chlorodibromo*-1:2:4-*triketohydronaphthalene-2′-carboxylic acid*,

$$\begin{array}{l} COOH{\cdot}C{:}CH{-\!-}C{\cdot}CO{\cdot}CO \\ \quad | \qquad\quad \| \qquad | \\ \quad CH{:}CBr{\cdot}C{\cdot}CO{\cdot}CBrCl \end{array},H_2O,$$

is obtained along with the dichlorobromo-acid when chlorine acts on dibromhydroxynaphthaquinonecarboxylic acid suspended in chloroform; it becomes yellow and sinters at 160°, melting at 253°. It is readily converted into chlorobromhydroxyhydrindenecarboxylic acid, which is formed on crystallising it from dilute mineral acids; hot glacial acetic acid gives rise to chlorobromhydroxynaphthaquinonecarboxylic acid, but this change also involves the production of hydroxyindenecarboxylic acid.

3:4:3:4′-*Dichlorodibromo*-1:2-*diketohydronaphthalene-2′-carboxylic acid* is produced when chlorine acts on dibromo-β-naphthaquinonecarboxylic acid suspended in glacial acetic acid; it is also formed from the quinone, and when the latter is used, chloroform may be employed instead of acetic acid. It crystallises from glacial acetic acid on the addition of concentrated hydrochloric acid, and separates from nitric acid of sp. gr. = 1·4 in rosettes of small needles, containing $1H_2O$, which is removed above 100°; it melts and slowly decomposes at 150°. Water and a solution of sodium acetate dissolve the substance without change if gently heated, but decomposition occurs on boiling the liquid; caustic soda and sodium carbonate hydrolyse the diketone forming dichlorodibromo-1′-hydroxyhydrindene-2:1′-dicarboxylic acid (see below). The diketone is indifferent towards oxidising agents, but stannous chloride reduces it to 3:4′-chlorobromo-β-naphthaquinone-2′-carboxylic acid, which rapidly passes into the quinol; more energetic action converts it into 4′-bromo-1:2-naphthaquinone-2′-carboxylic acid. When the substance is heated at 175—180°, it reddens,

and liberates halogen, yielding chlorobromo-β-naphthaquinonecarboxylic acid.

3:4′-*Chlorobromo-2-hydroxy-a-naphthaquinone-2′-carboxylic acid* is obtained from the foregoing diketone by dissolving it in hot, glacial acetic acid, adding an equal volume of concentrated sulphuric acid, and gently heating the liquid; it is also produced by the action of very dilute caustic soda on chlorobromo-β-naphthaquinonecarboxylic acid or its quinol. It separates from glacial acetic acid in pale yellow crystals containing 1 mol. of the solvent, and does not melt below 290°, although it sinters at this temperature; the *sodium* salt is sparingly soluble, and crystallises in beautiful, red needles.

2′:3′:4:2′-*Dichlorodibromo-1′-hydroxyhydrindene-2:1′-dicarboxylic acid*, $COOH\cdot C_6H_2Br<\begin{matrix}C(OH)(COOH)\\ \text{———}CHCl\text{———}\end{matrix}>CBrCl$, is obtained, as stated above, by the action of sodium carbonate on 3:4:3:4′-dichlorodibromo-1:2-diketohydronaphthalene-2′-carboxylic acid, and is sparingly soluble in alcohol, ether, acetic acid, and chloroform; it crystallises from a mixture of glacial acetic and concentrated hydrochloric acids in thin plates, and melts, decomposing, at 242°. When treated with boiling water, carbonic anhydride is eliminated, and the substance is converted into 2′:4-*chlorobromo-1′-ketohydrindene-2-carboxylic acid*, $COOH\cdot C_6H_2Br<\begin{matrix}CO\\CH\end{matrix}\geqslant CCl$, which crystallises from dilute acetic acid in elongated, yellow leaflets, and gradually chars at 250°; chlorine converts it into 2′:2′:3′-*trichloro-4-bromo-1′-ketohydrindene-2-carboxylic acid*, $COOH\cdot C_6H_2Br<\begin{matrix}-CO-\\CHCl\end{matrix}>CCl_2$, which crystallises from nitric acid of sp. gr. = 1·4 in colourless leaflets, and melts at 230°.

2′:3′:4:2′-*Dichlorodibromo-1′-ketohydrindene-2-carboxylic acid*,

$$COOH\cdot C_6H_2Br<\begin{matrix}-CO-\\CHCl\end{matrix}>CBrCl,$$

is produced when the foregoing hydroxycarboxylic acid is dissolved in hot glacial acetic acid and oxidised with chromic acid; it crystallises from nitric acid in slender needles, and melts at 205—206°. 2′:3′:4-*Dichlorobromo-1′-ketoindene-2-carboxylic acid*,

$$COOH\cdot C_6H_2Br<\begin{matrix}CO\\CCl\end{matrix}\geqslant CCl,$$

is obtained by treating it with excess of sodium carbonate, and acidifying the yellow solution with hydrochloric acid; the yellow *sodium* salt is sparingly soluble, and the *anilide* is red.

The *lactone* of 4-a-bromo-β-hydroxypropionyl-5-bromisophthalic acid, $COOH\cdot C_6H_2Br<\begin{matrix}CO\text{————————}\\CH(CHBr\cdot COOH)\end{matrix}>O,H_2O$ is produced along with dibromhydroxynaphthaquinonecarboxylic acid by the action of alkali on dibromo-β-naphthaquinonecarboxylic acid; it crystallises from nitric and dilute hydrochloric acids in lustrous leaflets, melts and decomposes at 224°, above which temperature it solidifies, and finally fuses about 280°. Although indifferent towards acidic oxidising agents, it is converted into bromotrimellitic acid by potassium per-

manganate or a solution of bleaching powder. The *dimethylic* salt crystallises from methylic alcohol in colourless prisms, and melts at 168°.

The *lactone* of 4-β-hydroxypropionyl-5-bromisophthalic acid,

$$COOH\cdot C_6H_2Br<\begin{matrix}CO\text{———————}\\CH(CH_2\cdot COOH)\end{matrix}>O,$$

is obtained by heating the foregoing substance with hydriodic acid and red phosphorus for 1½ hour at 160°; it crystallises from nitric acid in small, colourless needles, and melts at 275—276°. The *barium* salt forms slender needles, containing $3H_2O$; the *dimethylic* salt crystallises in leaflets, and melts at 102°.

Asymmetric propionylisophthalic acid is obtained by reducing bromhydroxypropionylbromisophthalic acid in aqueous solution with 4 per cent. sodium amalgam, and separates from glacial acetic or nitric acid in colourless crystals melting at 265—266°.

4-*Acetyl-5-bromisophthalic acid* is produced when the lactone of bromhydroxypropionylbromisophthalic acid is heated with very dilute aqueous barium hydroxide; it crystallises from water, and melts at 224—225°. The *dimethylic* salt crystallises from methylic alcohol in rosettes of small needles, and melts at 114—115°.

Asymmetric ethylisophthalic acid is obtained by the prolonged action of sodium amalgam on acetobromisophthalic acid, and crystallises from hot water; it becomes brown and melts at 266—267°.

M. O. F.

A Correction [Diamidonaphthalenesulphonic Acids]. By PAUL FRIEDLÄNDER and W. H. KIELBASINSKI (*Ber.*, 1896, **29**, 2574).—In the preparation of the two naphthylenediaminedisulphonic acids [1 : 3′ : 4 : 1′] and [1 : 3′ : 3 : 1′] from 1 : 3′-naphthylenediamine, the formulæ were exchanged through an error, so that for the compound [1:3′:4:1′], the compound [1:3′:3:1′] should be read, and *vice versâ.*

Further, it is now stated that the naphthalene-1 : 4′-disulphonic acid is readily isolated by means of its sodium salt which is sparingly soluble in a solution of sodium chloride.

J. F. T.

Essence of Angelica archangelica. By FELICE GIORDANI (*Gazzetta*, 1896, **26**, ii, 315—326). The essential oil of angelica (*Angelica archangelica*) is a limpid, heavy, reddish liquid of neutral reaction, which slowly deposits crystals consisting of a *substance*, $C_{32}H_{62}O_5$; the crystals are broad, yellow scales, melting at 74—77°. After fractionally distilling the oil under reduced pressure, a solid residue remains in the flask which, when washed with ether and crystallised from hot alcohol, yields a neutral *substance* of the empirical composition $C_7H_{13}O$; it forms small, white crystals, melting at 68—70°.

The distillate from the oil, when hydrolysed with alcoholic potash and distilled in a current of steam, yields a terpene-like oil, boiling at 240—270°, and evidently a mixture; the residue in the

distilling flasks contains the potassium salts of methylethylacetic acid and of a *hydroxypentadecylic acid*, $C_{15}H_{30}O_3$. The latter acid, when purified by crystallisation from petroleum, is obtained in aggregates of minute needles melting at 84°; its *barium* salt $(C_{15}H_{29}O_3)_2Ba$, forms a heavy, white precipitate. The acid readily yields an *acetyl* derivative, $C_{15}H_{29}O_3Ac$, which crystallises in pearly scales, melting at 59°.

Bromopentadecylic acid, $C_{15}H_{29}BrO_2$, is prepared by heating the hydroxy-acid at 100° with hydrobromic acid; it crystallises in minute pearly scales, melting at 65°. *Iodopentadecylic acid*, $C_{15}H_{29}IO_2$, obtained by heating the hydroxy-acid at 160° with hydriodic acid, is similar to the preceding acid in appearance and melts at 78—79°.

Hydroxypentadecylic acid is not present in the free state in the essence, but as an alkylic salt; traces of a phenolic substance were also found in the oil. W. J. P.

Ethereal Oils. Palmarosa Oil. By EDUARD GILDEMEISTER and KARL STEPHAN (*Arch. Pharm.*, 1896, **234**, 321—330).—This oil, formerly known as Turkish geranium oil, is prepared in the province of Bombay by distilling with water the leaves of a grass, *Andropogon Schoenanthus, L.* The sp. gr. of the purer samples examined varied between 0·888 and 0·896, and their rotation (in a 100 mm. tube) between +1°40′ and −1°55′. They were all soluble in three times their weight of 70 per cent. (by volume) alcohol, and this solubility affords a convenient means of detecting impurities, many of which are insoluble in alcohol of this strength. The commonest impurity is at present paraffin—of five samples from the London Docks all contained this substance, two of them to the extent of 50 and 90 per cent. respectively. The purer oil contains 1 per cent. of dipentene, with perhaps a trace of methylheptenone; also 12—20 per cent. of ethereal salts of acetic and normal caproic acids. The alcohol of these salts is, no doubt, geraniol, as this is the only alcohol that has hitherto been detected in the oil under examination. C. F. B.

Orientation in the Terpene Series: Pinene. By ADOLF VON BAEYER (*Ber.*, 1896, **29**, 2775—2796. Compare Abstr., 1896, i, 245, 308, and 620.)—The α-oxime of pinonic acid has been already described (Abstr., 1896, i, 246), and is an inactive substance which melts at 150°; it is prepared from α-pinonic acid, the solid product of oxidation of pinene, and the syrupy mother liquor from which α-pinonic acid has been separated, when treated with hydroxylamine yields two oximes, isomeric with the first. Of these the β-oxime, which melts at 128°, is identical with the substance obtained by Tiemann and Semmler from their liquid pinonic acid (Abstr., 1895, i, 478); it is dextrorotatory, and 1 decimetre of an 8·2 per cent. solution in ether has $\alpha = 2°18'$. The *γ-oxime* is less readily soluble than the β-modification, and separates from glacial acetic acid as a microcrystalline powder, melting at 190°—191°; it is lævo-rotatory in almost the same degree as the β-oxime is dextrogyrate, and 1 decimetre of a 2·8 per cent. solution in methylic alcohol has $\alpha = 47·5'$.

Pinarin, $C_{10}H_{14}O_3$, is slowly deposited in crystals from that fraction of the neutral product of oxidation of pinene which boils at 150—180° under a pressure of 15 mm.; it crystallises from hot petroleum in concentric aggregates of long needles melting at 66—68°, and has the properties of a lactone.

Hydroxyhomopinic acid,

$$COOH\cdot CH_2\cdot CH<{}^{CMe_2}_{CH_2}>CH\cdot CH(OH)\cdot COOH,$$

is obtained by reducing an alkaline solution of pinoylformic acid (Abstr., 1896, i, 621) with sodium amalgam; it crystallises from water in rhombic leaflets, and melts at 130°—133°. The *silver* salt is a crystalline powder which dissolves readily in water; the *copper* salt is bright blue.

a *Ketoisocamphoronic acid* (*dimethyltricarballoylformic acid*),

$$COOH\cdot CO\cdot CMe_2\cdot CH(COOH)\cdot CH_2\cdot COOH,$$

is produced when sodium hypochlorite or hypobromite acts on pinoylformic acid; it crystallises from water in six and eight-sided plates and leaflets, and melts, evolving gas, at 186—187°. The *silver* salt crystallises from water in minute needles; copper acetate produces no insoluble salt, and on heating the liquid cuprous oxide is precipitated. When the aqueous solution is heated with lead peroxide, dimethyltricarballylic acid is produced; the anhydro-acid melts at 145—146°, and when treated with boiling water yields dimethyltricarballylic acid melting at 149—151°, a specimen which had been heated with water at 230° melting at 156—157° (compare Tiemann and Semmler, Abstr., 1895, i, 478).

When α-ketoisocamphoronic acid is reduced with sodium amalgam, the *lactone* of α-hydroxyisocamphoronic acid,

$$\begin{array}{l}COOH\cdot CH\cdot CMe_2\cdot CH\cdot CH_2\cdot COOH,\\ \quad\quad\;\; | \quad\quad\quad\quad\;\; | \\ \quad\quad\;\; O\text{———}CO\end{array}$$

is formed; it crystallises from water in thick prisms containing $1H_2O$, and sinters at 160°, solidifying as the temperature rises, and finally melting at 185—186°. On heating the lactone with hydriodic acid during 4 hours at 170°, it is converted into isocamphoronic acid, which therefore has the constitution

$$COOH\cdot CH_2\cdot CMe_2\cdot CH(COOH)\cdot CH_2\cdot COOH,$$

an expression which does not agree with the formula of Bredt and Tiemann.

The *lactone* of α-hydroxydimethyltricarballylic acid,

$$\begin{array}{l}CMe_2\cdot CH\cdot COOH\\ | \quad\quad\;\; | \\ CO\cdot O\cdot CH\cdot COOH\end{array},$$

is obtained by brominating dimethyltricarballylic acid with phosphorus tribromide and bromine, and allowing the product to fall into boiling water; it separates from ethylic acetate in very large crystals, and melts at 196° when slowly heated, and at 207° when the temperature is

raised rapidly, much gas being evolved. The *calcium* salt crystallises in needles containing $3H_2O$, and when dried at 125° contains $1H_2O$; the *barium* salt is similar, and the *silver* salt crystallises in short needles. Fusion of the lactonic acid with potash gives rise to oxalic and *as*-dimethylsuccinic acids.

Valuable theoretical conclusions are drawn from the foregoing observations and those already recorded. Wagner's formula for pinene is still supported, and the breaking down of a molecule having this structure is traced through its various phases, represented by the production of pinonic, pinoylformic, pinic, and norpic acids. The last-named substance, $COOH{\cdot}CH{<}{}^{CMe_2}_{CH_2}{>}CH{\cdot}COOH$, is a derivative of the dimethylated tetramethylene residue, which the author calls the picean-ring. M. O. F.

Orientation in the Terpene Series: Caronic Acid. By ADOLF VON BAEYER and WLADIMIR IPATIEFF (*Ber.*, 1896, **29**, 2796—2802).—In view of the stability of the trimethylene-ring towards alkaline permanganate, carone, which according to von Baeyer has the constitution, $\begin{matrix} CHMe{\cdot}CO{\cdot}CH \\ | \qquad\quad | \\ CH_2{-}CH_2{\cdot}CH \end{matrix}{>}CMe_2$ (Abstr., 1896, i, 246), has been submitted to oxidation with this agent; caronic acid, a dimethyltrimethylene-1 : 2-dicarboxylic acid, capable of existing in *cis*- and *trans*-modifications, has been thus obtained.

The *caronic acids*, $CMe_2{<}\begin{matrix} CH{\cdot}COOH \\ | \\ CH{\cdot}COOH \end{matrix}$, are produced when carone is heated in a reflux apparatus on the water bath with potassium permanganate for 36 hours; after removing oxalic acid, the neutral liquid is extracted with ether, acidified, and again extracted, the acid syrup obtained in this manner depositing the *cis*-acid in crystals, the *trans*-modification being isolated by conversion into the ammonium salt.

cis-*Caronic acid* (cis-*dimethytrimethylene*-1 : 2-*dicarboxylic acid*) crystallises from water in plates, and melts at 174—175°; it is almost soluble in chloroform, and dissolves but sparingly in ether and petroleum. The *ammonium* salt is precipitated in needles on adding ether to the alcoholic solution; the *calcium* and *silver* salts are amorphous. The *anhydride* is formed at the melting point of the acid, and after crystallisation from ether melts at 54—56°. When the acid is heated for 7 hours at 100° with a solution of hydrobromic acid saturated at 0°, it is converted completely into the isomeric terebic acid.

trans-*Caronic acid* crystallises from water in prisms, and melts at 212°, no gas being evolved below 245°; the *ammonium* salt crystallises from water in prisms, and the *silver* salt is sparingly soluble. This modification does not form an anhydride; it is converted into terebic acid under the same conditions as the *cis*-acid. M. O. F.

Methoethylheptanonolide melting at 64° (Homoterpenylic acid methyl ketone). By J. C. W. FERDINAND TIEMANN (*Ber.*, 1896, **29**, 2616—2621).—The oxime of methoethylheptanonolide (Wallach, Abstr., 1895, i, 548) crystallises in rhombs, and melts at

79—80°; when heated with concentrated sulphuric acid at 100°, it is converted into acetic acid, along with the base *methyl-2-aminoethyl-3-pentolide-2 : 5*, $\underset{\displaystyle CMe_2\text{---}O}{NH_2\cdot CH_2\cdot CH_2\cdot \overset{|}{C}H\cdot CH_2\cdot \overset{|}{C}O}$. This result establishes the formula for methoethylheptanonolide already put forward (*loc. cit.*); and although it apparently favours von Baeyer's formula for pinonic acid, the author continues to advocate the expression

$$CHMe{<}\begin{matrix} CMe_2\cdot CH\cdot CH_2\cdot COOH \\ \quad | \\ CO\text{---}CH_2 \end{matrix}$$

(Abstr., 1895, i, 478). M. O. F.

Preparation of Terpenylic and Terebic Acids. By FRIEDRICH MAHLA and J. C. W. FERDINAND TIEMANN (*Ber.*, 1896, **29**, 2621—2622).—By oxidation with chromic and sulphuric acids, methoethylheptanonolide is converted without difficulty into terpenylic acid; when nitric acid is used as the oxidising agent, terebic acid is produced.

M. O. F.

Menthene Nitrosochloride and some of its Derivatives. By W. O. RICHTMANN and EDWARD KREMERS (*Amer. Chem. J.*, 1896, **18**, 762—779).—Owing to the varying statements with regard to the melting point of menthene nitrosochloride (compare Abstr., 1892, 1479; 1894, i, 468; *Ber.*, **26**, 2561), the authors have been induced to make a thorough study of the physical constants of menthene and its nitrosochloride. The menthene was prepared by the dehydration of menthol by means of hydrogen potassium sulphate or anhydrous copper sulphate, followed by careful fractionation. A table is given showing the boiling points, densities and specific rotatory powers of the various fractions obtained. The nitrosochloride was prepared by the gradual addition of a solution of 18 c.c. of concentrated hydrochloric acid in an equal volume of glacial acetic acid to a mixture of 45 c.c. of menthene, 45 c.c. of glacial acetic acid and 33 c.c. of ethylic nitrite placed in a freezing mixture. The product was submitted to repeated fractional crystallisation, the melting points, sp. rotatory powers and percentage yields of the various fractions being recorded in several tables. The results show that the nitrosochloride prepared by the above method is a mixture, and indicate the existence of a dextrogyrate, a lævogyrate and an inactive compound. Very little of the lævo-compound could be obtained. Three specimens of the nitrosochloride having specific rotatory powers differing by 30° all yielded optically inactive benzylamine bases. On heating with alcoholic potash, the dextrogyrate nitrosochloride yielded a lævogyrate nitrosomenthene, melting at 66·5—67·5° after re-crystallisation from alcohol. An inactive nitrosomenthene (m. p. 65—67°) was obtained from the inactive nitrosochloride. Menthylamine nitrate was prepared by the reduction of nitrosomenthene with acetic acid and zinc dust, but the yield was very small. The ketone, $C_{10}H_{16}O$, prepared by the action of hydrochloric acid on nitrosomenthene, boils at 207—208° (not 210—212°, as stated by Kremers and Urban). The nitrosomenthene from the mixed nitrosochlorides yielded a slightly lævogyrate

ketone, that from the inactive nitrosochloride a slightly dextrogyrate compound ($[\alpha]_D = -0{\cdot}3173°$ and $+0{\cdot}4299°$ respectively).

A crystalline *hydrosulphide* of the ketone was obtained, melting at 206—208°, which on analysis gave results nearly agreeing with the formula, $C_{10}H_{16}O,2H_2S$. By the application of Baeyer's method, a small quantity of the nitroso-derivative of the ketone was prepared, melting at 115—115·5°, but the yield was too small to admit of further work. A crystalline *hydrazone*, $C_{10}H_{16}{:}N_2HPh$, of the ketone was prepared, melting and evolving gas at 73·5—74°. It undergoes rapid decomposition in the air, gas being given off and a dark green, resinous mass remaining. When substituted phenylhydrazines were employed, no satisfactory results were obtained; negative results were also obtained in the attempt to prepare the nitrosochloride of the ketone. The reduction of the ketone by Beckmann's method was tried, when the chief products obtained were a yellow oil and a white, crystalline substance. The greater part of the oil boiled at 207—208°, and had sp. gr. = 0·9019 at 20° and $[\alpha]_D = -0{\cdot}8144°$. It therefore differed but slightly in its physical constants from the original ketone. A molecular refraction determination pointed to this oil being the alcohol $C_{10}H_{18}O$, but its chemical behaviour indicated that it consisted mainly of the unchanged ketone. The crystalline substance (m. p. 160—162°) gave analytical results which showed that it was neither the alcohol $C_{10}H_{18}O$ nor the corresponding pinacone. The investigation of these products will be continued. A. C. C.

Substances derived from Camphoroxime and Fenchone-oxime. By FRIEDRICH MAHLA and J. C. W. FERDINAND TIEMANN (*Ber.*, 1896, **29**, 2807—2824. Compare Abstr., 1895, i, 426).—The paper contains a more detailed account of the salts of camphorimine; the nitrate melts at 158—159°, and the base, which sublimes at the ordinary temperature, melts at 95°. The *hydrochloride* crystallises in long needles, and sublimes without melting when heated; the *auro-chloride* dissolves in ether.

Camphorimine becomes liquid when exposed to the air, and also under the influence of caustic alkalis, ammonia being eliminated; various agents resolve it into ammonia and camphor, this change taking place when the base is treated with boiling hydriodic acid. When distilled in an atmosphere of steam, the base passes over in the form of an oil, which boils at 104° under a pressure of 17 mm., yielding a mixture of the original base and a nitrile. An aqueous solution of the hydrochloride, if left for a considerable period, yields a feebly basic *compound*, $C_{30}H_{46}N_2$, which melts at 100°, and forms an *auro-chloride*.

Camphenylnitramine, contrary to the statement of Angeli (Abstr., 1895, i, 426) gives Liebermann's reaction; the potassium derivative is in part converted into camphorimine under the influence of alcoholic potash. The authors lay down their reasons for ascribing to camphenylnitramine the nitramine formula, and confirm the observations of Angeli and Rimini (*loc. cit.*) regarding the action of strong sulphuric acid on the substance. Isocamphor, the product of this change, yields a *semicarbazone* melting at 215°, and the *bisnitrosochloride* melts

at 120—121°. Reduction converts it into a dihydrogenised secondary alcohol, which is oxidised to *dihydroisocamphor*, a liquid boiling at 203°, the semicarbazone of which melts at 162°. Oxidation of isocamphor with potassium permanganate gives rise to a dibasic *acid*, $C_8H_{14}O_4$, which melts at 96°, and with acetic chloride yields the *anhydride*, melting at 60°. These results have led Angeli and Rimini to regard the acid as an isopropylglutaric acid, and they ascribe to isocamphor a constitution represented by one of the formulæ

$$\begin{array}{l} CH{:}CMe{\cdot}CO \\ \vert \qquad\qquad \vert \\ CH_2{\cdot}CH_2{\cdot}CHPr \end{array} \qquad\qquad \begin{array}{l} CH{:}CMe—CO \\ \vert \qquad\qquad \vert \\ CHPr{\cdot}CH_2{\cdot}CH_2 \end{array}$$

Fenchoneoxime melts at 163° (Wallach gives 148—149°), and when the ethereal solution is treated with nitrous acid, it yields the *nitrate* of fenchoneimine, $C_{10}H_{17}N,HNO_3$, which melts at 152°; the *hydrochloride* gives rise to fenchone when treated with sodium hydrogen sulphite. *Fenchonitrimine*, $C_{10}H_{16}N_2O_2$, corresponds with camphenylnitramine, and remains in the ethereal liquid after separation of fenchoneimine nitrate; it softens at 52°, and melts at 58°.

The paper concludes with some interesting theoretical observations.

M. O. F.

Camphoric Nitrile and Isomeric Change of Isonitrosocamphor. By GIUSEPPE ODDO and G. LEONARDI (*Gazzetta*, 1896, **26**, i, 405—423).—The substance which Oddo obtained by the action of acetic chloride on isonitrosocamphor (Abstr., 1893, i, 660) is found to be *camphoric β-mononitrile*, $CN{\cdot}C_8H_{14}{\cdot}COOH$, and owes its formation to an isomeric change of isonitrosocamphor; since the cyanogen radicle is attached to the methylene group contiguous to the ketonic carbon atom, the compound is termed a β-nitrile, in accordance with Claisen and Manasse's suggestion (Abstr., 1893, i, 479). It is also obtained on treating isonitrosocamphor with phosphorus pentachloride, phosphorus trichloride, or acetic anhydride; after evaporating the solvent, the residue is treated with water, dissolved in sodium carbonate, precipitated with hydrochloric acid, and crystallised from boiling water. It is colourless, melts at 151—152°, is soluble in alcohol, chloroform, ether or benzene, and is readily distinguished from its isomeride by giving a colourless solution in alkali, and by not yielding camphoquinone on treatment with sodium nitrite and acetic acid. The *silver* salt, $CN{\cdot}C_8H_{14}{\cdot}COOAg$, is a voluminous white powder, and is readily converted into the methylic salt, which crystallises in hard, transparent crystals, melting at 41—42°; the ethylic salt melts at 22—24°.

An ethereal solution of the nitrile absorbs dry hydrogen chloride yielding a white, crystalline hydrochloride, melting at 156—158°, identical with the α-camphorisoimide hydrochloride prepared by Hoogewerff and van Dorp (Abstr., 1896, i, 313) by the action of acetic chloride on β-camphoramic acid; the constitution,

$$C_8H_{14}<\begin{matrix}C(NH)\\CO\text{—}\end{matrix}>O,HCl,$$

assigned to it by the Dutch chemists is in agreement with the fact

that dry hydrogen chloride does not induce isomeric change in the methylic salt of the β-nitrile. The hydrochloride yields a *platinochloride*, $(C_{10}H_{15}NO_2)_2,H_2PtCl_6$, which crystallises in beautiful, yellow scales, and an *aurochloride*, which forms small, yellow crystals, melting at 130—140°; the hydrochloride, platinochloride, and aurochloride are slowly decomposed by water, yielding β-camphoramic acid.

Camphoric β-nitrile is converted into a mixture of camphoric acid and camphorimide by heating with fuming hydrochloric acid, and into camphorimide by sulphuric acid.

The *hydrochloride* of β-amidocampholic acid, $C_8H_{14}<\begin{smallmatrix}CH_2\cdot NH_2\\COOH\end{smallmatrix}$, is formed on reducing the mononitrile in absolute alcoholic solution with sodium and, after dilution with absolute alcohol, passing in a current of dry hydrogen chloride; after filtration, the filtrate is evaporated to dryness, and the residue crystallised from light petroleum; it crystallises in white needles, melting and decomposing at 268—270°, and gives a *platinochloride*, $(C_{10}H_{19}NO_2)_2,H_2PtCl_6$, which crystallises in yellow scales blackening at 270°. On heating the hydrochloride above its melting point, it is converted into an anhydride, $C_8H_{14}<\begin{smallmatrix}CH_2\\CO\end{smallmatrix}>NH$, which crystallises in colourless prisms melting at 228—230°.

The *anhydride*, $(CN\cdot C_8H_{14}\cdot CO)_2O$, of camphoric β-mononitrile is formed during the preparation of the mononitrile by the action of acetic anhydride or chloride on isonitroso-camphor, and is best prepared by treating a soda solution of the nitrile with acetic anhydride; it crystallises in colourless, transparent prisms, melting at 172—173°, is soluble in chloroform or alcohol, and when boiled with alcoholic potash and acidified yields the original nitrile.

The conversion of isonitroso-camphor into camphorimide by the action of sulphuric acid (Angeli, Abstr., 1893, i, 277) proceeds in two stages; β-camphoramic acid is first formed, and by the further action of sulphuric acid is converted into the imide. W. J. P.

NOTE BY ABSTRACTOR.—It should be noted that the β-derivatives mentioned in this paper are termed α-derivatives by Hoogewerff and van Dorp (*loc. cit.*).

Action of Nitrous Acid on Camphoroxime. By ANGELO ANGELI (*Gazzetta*, 1896, **26**, ii, 29—34. Compare Abstr., 1895, i, 426).—The author considers that pernitrosocamphor, $C_{10}H_{16}N_2O_2$, which is identical with Tiemann's camphenylnitramine, has not the constitution, $C_8H_{14}<\begin{smallmatrix}CH\\\Vert\\C\cdot NH\cdot NO_2\end{smallmatrix}$, assigned to it by the latter, but contains the group $:C:N_2O_2$. Tiemann supposes the first action of nitrous acid on camphoroxime to be the formation of camphoroxime nitrite, which then spontaneously changes into the isomeric camphorimine nitrate; this then loses water, giving camphenylnitramine or pernitrosocamphor.

A quantitative yield of pernitrosocamphor can be obtained by the action of nitrous acid on camphoroxime in very dilute solution; further, it may be conveniently prepared by dissolving camphoroxime

in amylic nitrite, when white needles of campherimine nitrite separate, leaving pernitrosocamphor in solution. On treating camphoroxime in sodium ethoxide solution with amylic nitrite, pernitrosocamphor is produced. These facts speak strongly against Tiemann's hypothesis respecting the formation of pernitrosocamphor, which requires the presence of free nitrous acid.

Campherimine nitrate should, according to Tiemann's view, readily yield an anhydride; but the author was unable to prepare such a compound, the nitrate crystallising unchanged from hot acetic anhydride. No nitric acid is obtained on treating the nitrate with concentrated sulphuric acid, although this reaction is characteristic of nitramines (Lachmann, "Ueber Nitroharnstoff, &c.," *Inaug. Diss. Munich*, 1895).

The yellow potassium salt of pernitrosocamphor melts at 43°, but on cautiously acidifying its aqueous solution and filtering, a yellow salt melting first at 57°, and after resolidification at 43°, is obtained; it differs from the salt melting at 43° by being readily soluble in dilute aqueous alkali. W. J. P.

Action of Nitrous Acid on Camphoroxime. By ANGELO ANGELI and ENRICO RIMINI (*Gazzetta*, 1896, **26**, ii, 34—45; 45—54. Compare preceding abstract).—The most convenient method of preparing camphoroxime consists in heating a mixture of camphor (175—200 grams), spirit (600 c.c.), hydroxylamine hydrochloride (100 grams) and caustic soda (140 grams) gradually on the water bath, then boiling for 4 hours, evaporating off most of the alcohol and pouring into water; after filtering off the deposited oxime, a further quantity can be obtained by exactly neutralising with hydrochloric acid.

Pernitrosocamphor (Abstr., 1895, i, 426) is best prepared by adding sodium nitrite to a solution of camphoroxime in dilute hydrochloric acid and recrystallising the deposited powder from alcohol; it crystallises in large, colourless crystals of characteristic odour, melts at 45°, and has the normal molecular weight in freezing benzene.

On treating it with concentrated sulphuric acid, pernitrosocamphor evolves nitric oxide, and on distilling the product in a current of steam, *isocamphor*, $C_{10}H_{16}O$, is obtained as an oil of pleasant odour, boiling at 216° under ordinary pressure with slight resinification; it slowly changes in the air, is resinified by alkalis, and immediately decolourises permanganate, but does not condense with benzaldehyde or ethylic formate. Its oxime melts at 106°, and is dissolved unaltered by concentrated sulphuric acid, but is readily hydrolysed by boiling with dilute sulphuric acid. Isocamphor, when treated with an alcoholic solution of semicarbazide acetate, yields a *semicarbazone*, melting at 215°.

Isocamphor bisnitrosochloride, $C_{10}H_{16}NO_2Cl$, is prepared by the action of acetic chloride on a mixture of isocamphor and amylic nitrite cooled in ice; it is deposited in small, white crystals, melting and decomposing at 120—121°, and its formation indicates that the isocamphor molecule contains a double bond.

On reducing isocamphor in alcoholic solution with sodium, distilling in a current of steam, and treating the oily product with permanganate to remove impurities, a *tetrahydroisocamphor* is obtained as a heavy,

colourless oil having a lavender-like odour. Chromic acid mixture converts it into a *dihydroisocamphor* which is obtained as a colourless oil of fruity odour boiling at 203°; its *semicarbazone*,

$$C_{10}H_{16}:N\cdot NH\cdot CO\cdot NH_2,$$

prepared by the aid of semicarbazide acetate, crystallises in thin, white needles melting at 162°, and when treated with dilute sulphuric acid yields pure dihydroisocamphor. The latter is stable towards permanganate, and does not condense with benzaldehyde, but gives a crystalline *compound* with sodium hydrogen sulphite.

On oxidising isocamphor with alkaline permanganate, it yields a dibasic *acid*, $C_8H_{14}O_4$, which crystallises in white needles, melting at 96°; determinations of its electrical conductivity give the values

$$K = 0{\cdot}00525 \text{ and } \mu\infty = 351,$$

which are characteristic of the glutaric acids. Its *anhydride*, $C_8H_{12}O_3$, formed on treating it with acetic chloride, crystallises in long, thin needles, melting at 60°. The acid of the composition, $C_8H_{14}O_4$, yields succinic acid when oxidised with a mixture of chromic and sulphuric acids, so that it most probably has the constitution

$$COOH\cdot CHPr\cdot CH_2\cdot CH_2\cdot COOH.$$

The most probable constitution at present assignable to isocamphor is the following

$$CH_2{<}{\substack{CH_2\cdot CH_2\\ CHPr\cdot CO}}{>}CMe.$$

Pernitrosocamphor is violently acted on by bromine, but on adding bromine to its glacial acetic acid solution saturated with dry hydrogen bromide, *bromopernitrosocamphor*, $C_{10}H_{15}BrN_2O_2$, slowly separates; it crystallises in long, colourless, lustrous needles, melting at 114°, and when treated with dilute alcoholic potash is converted into *isobromopernitrosocamphor*, $C_{10}H_{15}BrN_2O_2$, which separates from alcohol or petroleum in large, colourless crystals, melting at 67°. Both isomerides give off nitric oxide and hydrogen bromide when treated with concentrated cooled sulphuric acid, the iso-compound yielding *isocamphenone*, $C_{10}H_{14}O$, which separates from petroleum in yellowish crystals of pleasant odour, melting at 92°; it soon resinifies in the air, gives an *oxime* melting at 170°, and on reduction with alcohol and sodium seems to give tetrahydroisocamphor.

Dibromopernitrosocamphor, $C_{10}H_{14}Br_2N_2O_2$, may be prepared by treating a chloroform solution of pernitrosocamphenone with bromine; it separates from petroleum in large, white crystals, melting at 133°.

On treating camphenone with hydrogen bromide in glacial acetic acid solution, a new *bromocamphor*, $C_{10}H_{15}BrO$, is obtained; it is extremely stable towards acids, but is readily converted into camphenone by alkalis and yields camphenonoxime on treatment with alkaline hydroxylamine solution.

A new *dibromocamphor*, $C_{10}H_{14}Br_2O$, is obtained by treating camphenone with bromine in carbon bisulphide solution; it separates from alcohol or petroleum in large, colourless crystals melting at 58—59°.

It may be readily distinguished from ordinary dibromocamphor by treating it with alcoholic potash, when *bromocamphenone*, $C_{10}H_{13}BrO$, is produced; it forms large, colourless crystals melting at 70°, and has the curious property that on cooling its hot saturated solutions, all the substance separating collects in one large crystal.

Provisional constitutional formulæ for camphenone and its derivatives are proposed.

In a note appended to this paper, Angeli combats Aschan's views (Struktur und stereochemischen Studien in der Camphergruppe, Helsingfors, 1895) as to the structure of camphenone and monoketazocamphadione, and also the view that camphor contains the group $CO\cdot CH_2\cdot CH\colon$ W. J. P.

Action of Nitrous Acid on Oximes of the Camphor Series. By ANGELO ANGELI and ENRICO RIMINI (*Gazzetta*, 1896, **26**, ii, 228—229).—The results which the authors have obtained by the action of nitrous acid on camphoroxime have led them to extend the investigation to other oximes of the camphor series (Abstr., 1895, i, 426).

They find that camphenonoxime is converted into pernitrosocamphenone by nitrous acid. Menthonoxime, when treated with nitrous acid, yields an unstable liquid product which is decomposed by concentrated sulphuric acid with evolution of gas.

Fenchonoxime is converted by nitrous acid into a beautiful *pernitroso*-derivative which is decomposed by concentrated sulphuric acid yielding nitrous oxide and isocamphor. This fact seems to confirm the authors' view that isocamphor is a derivative of metacymene (compare this vol., i, 88). W. J. P.

Monoketazocamphadione. By ENRICO RIMINI (*Gazzetta*, 1896, **26**, ii, 290—292).—Monoketazocamphadione, $C_8H_{14}<\begin{matrix}CO\\|\\CN_2\end{matrix}$, combines with potassium hydrogen sulphite, yielding a *salt* of the composition $C_{10}H_{15}N_2SO_4K,2H_2O$, which is purified by precipitation from its aqueous solution by alcohol; it crystallises in lustrous, yellow scales, which do not decompose at 220°. When boiled with dilute hydrochloric acid, it gives azocamphanone, and when heated with concentrated hydrochloric acid in a current of steam, it yields azocamphanone, which decomposes, yielding camphadione; hydrazine hydrochloride is found in the solution.

The behaviour of monoketazocamphadione is thus similar to that of aliphatic diazo-compounds which combine with alkali hydrogen sulphites giving additive products which yield hydrazine on hydrolysis. W. J. P.

Derivatives of Dihydro-cis-campholytic Acid. By E. B. HARRIS (*Amer. Chem. J.*, 1896, **18**, 692—694).—The results of this investigation have already been described in a paper by Noyes (Abstr., 1896, i, 695). A. G. B.

Camphoric Acid. By WILLIAM A. NOYES (*Amer. Chem. J.*, 1896, **18**, 685—692. Compare Abstr., 1895, i, 187, 295, 552).—Most of the

results described have already appeared elsewhere (Abstr., 1896, i, 695).—*Ethylic amidolauronate* is a mobile, strongly basic liquid, with an ammoniacal, aromatic odour; its *sulphate*,

$$(NH_2 \cdot C_8H_{14} \cdot COOEt)_2, H_2SO_4,$$

was prepared.

Dihydro-cis-*campholytic acid* is prepared by reducing *cis*-campholytic acid with sodium in amylic alcohol; it is an oily liquid, smelling of valeric acid, boiling at 244°, almost insoluble in water, and of sp. gr. = 0·9833 at 20°; it is stable towards a cold solution of potassium permanganate. The *amide*, $C_8H_{15} \cdot CONH_2$, melts at 161°. *Cis*-campholytic acid boils at 255—256°, and *cis-trans*-campholytic acid at 240—243°.

a-Bromodihydro-cis-*campholytic acid* was prepared, after Baeyer's prescription (Abstr., 1888, 1075), from the dihydro-acid by treatment with phosphorus pentachloride and bromine. It crystallises from formic acid in needles and melts at 129—130°; when it is treated with cold alcoholic potash, *cis*-campholytic acid is regenerated.

Armstrong's formula for camphor is held to be disproved because *cis*-campholytic acid is not Δ^1-tetrahydroxylylic acid. A. G. B.

Constitution of Isocamphoronic acid. By J. C. W. FERDINAND TIEMANN (*Ber.*, 1896, **29**, 2612—2615).—The author ascribes to isocamphoronic acid the constitution $COOH \cdot CMe_2 \cdot CH(CH_2 \cdot COOH)_2$, because acetic chloride converts it into an anhydromonocarboxylic acid, which yields terpenylic acid under the influence of concentrated sulphuric acid; isocamphoronic acid also gives rise to terpenylic acid when treated with concentrated sulphuric acid, carbonic oxide being eliminated in each case.

Active α-dihydroxydihydrocampholenic acid, when oxidised, yields optically inactive isoketocamphoric acid, an observation which accords with the formula for the latter substance already suggested,

$$OMe \cdot CMe_2 \cdot CH(CH_2 \cdot COOH)_2.$$

M. O. F.

The Sap of Antiaris Toxicaria (Upas Tree). By HEINRICH KILIANI (*Arch. Pharm.*, 1896, **234**, 438—451).—Ether extracts *antiarol*, and some of the *resin*; the rest of the resin is removed by successive precipitations with alcohol; by concentrating the alcoholic solution and adding water, *antiarin* is obtained. The sap also contains a considerable amount of potassium nitrate.

Antiarol, $OH \cdot C_6H_2(OMe)_3$, forms white crystals, melting at 146°; it is identical with the 1 : 3 : 4 : 5 - hydroxytrimethoxybenzene (Will, *Ber.*, 1888, **21**, 612), and is thus closely related to the iretol of De Laire and Tiemann (Abstr., 1894, i, 48). Its *monobenzoyl* derivative melts at 117°.

Antiar-resin, perhaps $C_{24}H_{36}O$, crystallises in needles, and melts at 173·5°; it is chemically very inert.

Antiarin, $C_{27}H_{42}O_{10} + 4H_2O$, crystallises in rhombic or hexagonal plates, and softens at 220°, melting finally at 225°. It is a poisonous glucoside; indeed, the sap is used for poisoning arrows. When hydrolysed with dilute alcoholic hydrochloric acid, it is converted into

antiarigenin and antiarose. *Antiarigenin*, $C_{21}H_{30}O_5$, is a crystalline substance, and melts at about 180°, after first turning deep yellow at 180°. *Antiarose*, $C_6H_{12}O_5$, is isomeric with rhamnose; it was not isolated, but was oxidised with bromine and water to *antiaronic acid*, $C_5H_{11}O_4{\cdot}COOH$, the *lactone* and amorphous *calcium* salt of which were analysed. The lactone crystallises in prisms, and softens at 168°, melting finally at 180°; its specific rotation $[\alpha]_D = -30°$.

C. F. B.

Palm Dragon's-blood. By KARL DIETERICH (*Arch. Pharm.*, 1896, **234**, 401—437).—The dragon's-blood examined was a red substance imported in sticks ("*in bacillis*"), which form is less adulterated than the others, and was presumably derived from the fruits of *Daemonorops Draco* (Sumatra); it melted at 70°. If the crude resin is extracted with ether, and alcohol added, *dracoalban* is precipitated. If the ether alcoholic solution is then evaporated to dryness, light petroleum extracts *dracoresen* from the residue, and leaves a mixture of pure resins, of a red colour; this was shown to consist of the *dracoresinotannol* salts of benzoic and benzoylacetic acids. Of the above substances, the crude resin contains in 100 parts: dracoalban 2·5; dracoresen 13·58; red resin (mixture of ethereal salts) 56·86. In addition it contains a resin insoluble in ether, 0·33; a black, amorphous phlobaphene (an oxidation or decomposition product of a tannin; soluble in alkalis) 0·03; plant remains 18·40; ash 8·30.

Dracoalban, $C_{20}H_{40}O_4$, is a white, amorphous powder, becoming strongly electrified when rubbed; it softens at 192—193°, and blackens and decomposes above 200°. It is chemically rather inert, but yields a *trinitro*-derivative, which can be reduced to a *triamido*-derivative, and this yields a (mono?) *acetyl* derivative; these are all amorphous.

Dracoresen, $C_{26}H_{44}O_2$, is a bright yellow, amorphous resin, melting at 74°; it is chemically very inert. A possible indication was obtained of menthol among its products of hydrolysis.

The red resin consisted mainly of dracoresinotannol benzoate; the benzoylacetate was relatively small in amount. The *dracoresinotannol*, $C_8H_9O{\cdot}OH$, obtained from it on hydrolysis is a bright brown, amorphous powder; it softens at 100—105°, but then decomposes without melting. It yields a *potassium* and a *monacetyl* derivative, both brown and amorphous; nitric acid converts it into picric acid; and on dry distillation it yields benzene, toluene, and probably cinnamene and phenylacetylene, together with phenol, resorcinol, pyrogallol, and acetic acid, and possibly phloroglucinol and creosote. Other products of the hydrolysis of the resin, in addition to dracoresinotannol, are benzoic acid, acetic acid, and acetophenone, the two last coming respectively from the "acid" and "ketone decomposition" of the benzoylacetate. It is pointed out that the benzoylacetate can exist in a tautomeric form as a hydroxycinnamate, which suggests that it may have originated from the oxidation of a cinnamate, for some previous observers have found cinnamic acid in the crude resin.

C. F. B.

Zanzibar Copal. By STEPHAN (*Arch. Pharm.*, 1896, 234, 3, 552—560).—The crude resin was purified by the precipitation of its

alcoholic solution with water. The aqueous solution then contained a yellowish, bitter principle, which could not be obtained crystalline, and was not hydrolysed by dilute sulphuric acid. The resin was then dissolved in alcohol and ether, and extracted with dilute aqueous potash, two isomeric acids being thus removed, whilst an ethereal oil and two resins were left behind in the ethereal solution.

Trachylolic acid, $OH\cdot C_{54}H_{85}O_3(COOH)_2$, melts at 165°, but can be obtained in sphæro-crystals melting at 168°. It is only slightly soluble in acetone, ether, and chloroform, and is precipitated in alcoholic solution by lead acetate. It yields a *monacetyl* derivative which is only slightly soluble in carbon bisulphide, and a *monobenzoyl* derivative. The analysis of its potassium and copper salts shows that it is probably dibasic. The isomeric *isotrachylolic acid* is also a dibasic hydroxy-acid. It melts at 105—107°, is readily soluble in acetone, &c., and in alcoholic solution is not precipitated by lead acetate. The *acetyl* derivative is soluble in carbon bisulphide.

a-Copal-resen, $C_{41}H_{68}O_4$, melts at 75—77°, is insoluble in potash, soluble in ether, and does not yield an acetyl derivative. Its alcoholic solution has a rotation of $\alpha = +12\cdot56°$. *β-Copal-resen* is insoluble in ether, and decomposes at 140° without melting, The resin contains 80 per cent. of trachylolic acid, 4 per cent. of the isomeride, and 6 per cent. of the resens. A. H.

Resin of Gutta Percha. By GABRIELE TASSINARI (*Gazzetta*, 1896, **26**, ii, 248—256).—The resin of gutta percha, after extracting the gummy matter by alcohol, dissolves in concentrated soda, and on distilling the solution at 160—180°, a liquid (1) passes over. The residue when extracted with water gives a red liquid in which a flocculent precipitate (2) is suspended ; on acidifying the mother liquor with hydrochloric acid, a dark-coloured resin (3) sinks, whilst a flocculent precipitate (4) forms in the liquid. The mother liquor, on distillation under reduced pressure, gives an acid distillate (5) and a residue (6) which on extraction with alcohol becomes colourless; after distilling off the alcohol from the extract, a liquid residue is obtained, consisting of an upper layer (7) of fruity odour, and a lower one (8).

The liquid (1) consists of two layers of which the lower is a dilute aqueous solution of methylic alcohol, whilst the upper contains a *limonene*, $C_{10}H_{16}$, and an aldehyde, $C_{10}H_{16}O$, probably geranaldehyde. The limonene does not give a solid bromide or hydrochloride, and when treated with amylic nitrite and hydrogen chloride yields a crystalline *substance* melting and decomposing at 84°. The soft dark product (2) after being freed from a black oil by treatment with benzene, yields a white, crystalline, neutral *substance*, $C_{10}H_{20}O_2$, which melts and decomposes at 270°. The product (3) is a dark, soft resin, soluble in alcohol, ether, benzene, acetic acid and alkali carbonates, and constitutes about two-thirds of the original resin ; it carbonises on heating, and when treated with zinc dust gives a black oil which seems to contain homologues of benzene.

The fraction (4) when crystallised from benzene yields, when purified, a "*xyletinic acid*," $C_9H_{10}O_3$, in lustrous, colourless crystals, melting at 156—157°. Acetic acid was separated from the product

(5), and fraction (6) contains isouvitic acid. The liquid (7) yields isouvitic acid and probably geranaldehyde; the latter gives isogeranic acid on oxidation. W. J. P.

Raphanol, a substance contained in the root of Raphanus niger, and other Cruciferæ. By HENRI MOREIGNE (*J. Pharm.*, 1896 [6], 4, 10—16).—From the distillate obtained from the aqueous extract of the root of *Raphanus niger* the author isolated a crystalline substance, *raphanol*, $C_{29}H_{58}O_4$, which melts at 62°, decomposes about 300°, and is soluble in ether, chloroform, benzene, and light petroleum. It appears to be the lactone of an acid, but contains hydroxyl groups as it yields an *acetyl* derivative, melting at 122—123°. Lack of material prevented the author from carrying the investigation further. M. W. T.

A Glucoside contained in Adonis æstivalis, L. By NICOLAI KROMER (*Arch. Pharm.*, 1896, **234**, 452—458).—After the plant had been extracted with 96 per cent. alcohol at 60°, the alcoholic extract was evaporated down under diminished pressure, and extracted successively with light petroleum, ether, and chloroform. Chloroform extracted a new glucoside, $C_{25}H_{40}O_{10}$; this is a yellow, amorphous substance, very soluble in water and bitter to the taste; it is contained in the plant to the extent of 0·22 per cent. Its physiological action resembles that of the adonidin of *Adonis vernalis*, but is very much weaker. C. F. B.

Quercetin and its Derivatives. By JOSEF HERZIG (*Monatsh.*, 1896, 421—428. Compare Abstr., 1895, i, 387, 554, &c.).—The melting point of tetracetylluteolin is 223—226°, and not, as is stated by A. G. Perkin (Trans., 1896, 210), 213—215°. The author prepares triethylluteolin from its acetyl derivative, which is readily hydrolysed and has a molecular weight of 408, that calculated from the formula $C_{15}H_6O_6Et_3Ac$ being 412. Triethylluteolin (luteolin triethyl ether) is yellow, as Perkin has stated (*ibid.*, 800); it melts, however, at 140—143°, and not at 131—132°. The substance obtained from the crude extract does not appear to be the same as that prepared by the direct ethylation and acetylation of luteolin.

When diethyleuxanthone is warmed with concentrated sulphuric acid, complete decomposition ensues, and *fisetinsulphonic acid*,

$$C_{15}H_9O_6\cdot SO_3H,$$

is formed. This may be obtained directly from fisetin, but is most readily prepared by heating the alkylfisetins with about 10 times their weight of sulphuric acid during 4—5 hours on the water bath; it crystallises in beautiful, yellow needles, does not melt at 300°, dissolves readily in alcohol and water, but is insoluble in ether; its aqueous solution gives a green coloration with ferric chloride.

The author states that he is continuing the investigation of morin, and also the work of Cimiacian and Silber on the constitution of maclurin. A. L.

Digitoxin. By HEINRICH KILIANI (*Arch. Pharm.*, 1896, **234**, 481—489. Compare Abstr., 1896, i, 59, ii, 552). The substance previously described as β-digitoxin by the author is identical in all respects with Schmiedeberg's digitoxin. The supposed difference between the composition of the two has been found to be due to the difficulty with which digitoxin undergoes complete combustion. When hydrolysed with alcoholic hydrogen chloride, it yields digitoxigenin and digitoxose. The former of these melts at 225—230°, and, like digitoxin, is difficult to burn; it yields a crystalline *potassium salt*, $C_{22}H_{31}O_4K$, and crystalline precipitates with the chlorides of barium and calcium, and the author now proposes for it the formula $C_{22}H_{32}O_4$ instead of $C_{21}H_{32}O_4$. Digitoxose crystallises in prisms or tablets, melts at 101°, and has a rotation $[\alpha]_D = +46°$; its empirical formula is $C_3H_6O_2$, as previously found, and its molecular formula is probably $C_9H_{18}O_6$, although this requires experimental confirmation. It follows from this that the formula for digitoxin is $C_{31}H_{50}O_{10}$. Experiments carried out with the seeds of Digitalis show that digitoxin does not itself occur in these. A. H.

Pyridine Alkyl Hydroxides. By ALBERT B. PRESCOTT and S. H. BAER (*J. Amer. Chem. Soc.*, 1896, **18**, 247—251).—Pyridine propiodide (Abstr., 1896, i, 316), on treatment with moist silver oxide, yields a solution of *pyridine propohydroxide*, which precipitates salts of lead, silver, copper, iron, aluminium, chromium, cobalt, and nickel, an excess of the hydroxide solution redissolves the precipitates obtained with lead and aluminium. The solution also gives an alkaline reaction with litmus, phenolphthaleïn, brazil-wood, cochineal, hematoxylin or methyl-orange. Pyridine itself does not give an alkaline reaction with phenolphthaleïn or hematoxylin. The solution acquires a red colour when heated, and on evaporation yields a black residue, which is soluble in water. *Pyridineisopropohydroxide* has also been prepared. It resembles the normal compound in all the above-mentioned details. The *carbonate, sulphate* and *platinochloride* were obtained in a crystalline form. J. J. S.

α-Acetoacetylpyridyl [2-Acetoacetylpyridine]. By KARL MICKO. (*Montash.*, 1896, **17**, 442—461).—Ethylic picolinate and acetone condense when treated in the manner described by Weidel (compare this vol., i, 104). The product, *α-acetoacetylpyridine*, $C_5NH_4{\cdot}CO{\cdot}CH_2{\cdot}COMe$, crystallises in monoclinic needles or transparent prisms; $a:b:c = 0{\cdot}4679:1:0\,4824$, $\beta = 82°2'$. It melts at 49—50°, is volatile at elevated temperatures, slight sublimation occurring at the ordinary temperature, and dissolves readily in alcohol, ether, chloroform, benzene and boiling light petroleum but is insoluble in water. Its alcoholic solution, when mixed with ferric chloride, gives the red coloration characteristic of β-diketones. The *hydrochloride* crystallises in clear hygroscopic crystals and decomposes, evolving irritating vapours at 100°. The *platinochloride*, $(C_9H_9NO_2)_2,H_2PtCl_6 + 2H_2O$, forms yellowish-red tables and is exceedingly unstable. The diketone yields two *compounds* with mercuric chloride; the first is obtained when a strongly acid alcoholic solution of the base is mixed with an

alcoholic solution of mercuric chloride, and forms small, shining pyramidal crystals of the composition $C_9H_9NO_2,HCl,HgCl_2 + 2H_2O$, the second substance is produced on warming the foregoing compound with 60—70 per cent. alcohol, and forms silky, colourless needles which have the formula $C_9H_9NO_2,HgCl_2$.

α-Acetoacetylpyridine is decomposed into acetone and picolinic acid when heated with concentrated potash or soda. When warmed with phenylhydrazine acetate, it yields 3-*pyridyl*-1-*phenyl*-5-*methylpyrazole*, $NPh<\begin{matrix}N = C\cdot C_5NH_4 \\ \quad\ | \\ CMe{:}CH\end{matrix}$, which forms a yellowish, thick oil, distils at 215° under 15 mm. pressure, and does not solidify at −20°; it is insoluble in water and light petroleum, but dissolves readily in alcohol and ether. The *ethiodide*, $C_{15}H_{13}N,EtI$, forms lemon-yellow aggregates of leaves, and melts and decomposes at 181—183°; on shaking with silver chloride, the corresponding *chloro*-compound is obtained in the form of deliquescent needles; it yields a *platinochloride*,

$$(C_{15}H_{13}N_3)_2,Et_2PtCl_6,$$

which crystallises in dark orange-red grains.

Two compounds are obtained on treating α-acetoacetylpyridine with hydroxylamine, namely, a *monoxime*, $C_9H_{10}N_2O_2$, and a *dioxime*, $C_9H_{11}N_3O_2$, the monoxime is produced when the calculated quantity of sodium hydroxide is used, and forms crystals melting at 78° (uncorr.); it dissolves readily in alcohol, ether and hot chloroform. When treated with acetic acid saturated with hydrogen chloride, it suffers isomeric change, being converted into a *substance* which crystallises from boiling light petroleum in prisms melting at 48° (uncorr.); the new compound forms a deliquescent *hydrochloride*, is insoluble in water but dissolves readily in alcohol, and is doubtless an isoxazole derivative of the constitution $\begin{matrix}C_5NH_4\cdot C{:}CH\cdot CMe \\ \quad\quad | \qquad\ \ \| \\ \quad\quad O\text{——}N\end{matrix}$ The *dioxime* is produced when the monoxime is treated with excess of hydroxylamine in presence of free hydrochloric acid; it crystallises from hot water in small, four-sided prisms melting at 146—147° and decomposing at about 150° with evolution of gas; when treated with acetic acid and hydrogen chloride, it yields an *isoxazole* derivative isomeric with that obtained from the monoxime by a similar process. This substance crystallises from cold, light petroleum, in which it is readily soluble, in shining prisms melting at 37·5°; it yields a *hydrochloride* which separates from water in the form of aggregates of needles; its constitution is possibly represented by the formula $N<\begin{matrix}O\text{——}C\cdot C_5NH_4 \\ \qquad \| \\ CMe\cdot CH\end{matrix}$.

Ammonia acts on the diketone with production of, in the first instance, an *ammonium* compound, $C_5NH_4\cdot CO\cdot CH(NH_4)\cdot COMe$, which separates from the alcoholic solution as a fine crystalline precipitate, but decomposes when heated at 110—120° with production of the *amido*-derivative, $C_5NH_4\cdot CO\cdot CH{:}CMe\cdot NH_2$. The latter separates from alcohol in monoclinic tables; $a:b:c = 0·7004:1:0·9785$; $\beta = 71°54'$. It dissolves readily in alcohol and boiling water, but is insoluble

in benzene and petroleum, and melts at 149—150°; it reacts with phenylhydrazine and hydroxylamine, and is decomposed at the ordinary temperature by dilute hydrochloric acid with production of ammonium chloride and α-acetoacetylpyridine hydrochloride.

The diketone is reduced by zinc dust and acetic acid, a *substance* $C_9H_{11}NO_2$, crystallising in colourless needles, being formed. This melts at 74°, is readily soluble in water, alcohol, ether and ethylic acetate, but is insoluble in light petroleum; it yields a *platinochloride*,

$$(C_9H_{11}NO_2)_2,H_2PtCl_6,$$

in beautiful, orange-red crystals; when treated with hydroxylamine, it forms an *oxime*, $C_9H_{12}N_2O_2$, melting at 120°, and crystallising in small prisms readily soluble in alcohol and ether but insoluble in light petroleum; on oxidation with potassium permanganate, it yields picolinic and acetic acids, but, on treatment with alkali, it yields neither picolinic acid nor acetone as does the original diketone. These facts are all in accordance with the supposition that the reduction product is a ketonic alcohol having the formula $C_5NH_4\cdot CH(OH)\cdot CH_2\cdot COMe$.

A. L.

β-Benzoylpicolinic Acid and β-Pyridyl Phenyl Ketone. By BERTHOLD JEITELES (*Monatsh.*, 1896, **17**, 515—527).—The author describes in detail the preparation of β-benzoylpicolinic acid (compare Abstr., 1887, 737). The *hydrogen silver* salt,

$$COPh\cdot C_5NH_3\cdot COOAg,COPh\cdot C_5NH_3\cdot COOH,$$

crystallises in thick prisms, and is not affected by light.

Anti-*β-pyridylphenylketoxime*, $\begin{array}{c}Ph\cdot C\cdot C_5NH_4,\\ \| \\ N\cdot OH\end{array}$ is prepared by the action of hydroxylamine on the crude product obtained by heating β-benzoylpicolinic acid at 147—150°; it is insoluble in water, but dissolves readily in hot alcohol, and forms aggregates of crystalline granules; it sinters at 136°, and melts at 141—143°. When dissolved in ether and digested during 30 hours with phosphorus pentachloride, it yields a product melting at 59—60°, which, on hydrolysis, yielded benzoic acid and an oil; the latter commenced to distil at the boiling point of β-amidopyridine, but consisted, for the most part, of β-pyridyl phenyl ketone produced by the hydrolytic action of the hydrogen chloride on the oxime. The production of benzoic acid supplies the necessary proof of the configuration of the oxime.

Syn-*β-pyridylphenylketoxime*, $\begin{array}{c}Ph\cdot C\cdot C_5NH_4,\\ \| \\ HO\cdot N\end{array}$ is obtained when $2\frac{1}{2}$ molecular proportions of hydroxylamine are employed; this also is insoluble in water and readily soluble in hot alcohol, but it crystallises in stout prisms melting at 162—163°. When dissolved in dilute hydrochloric acid and reprecipitated by sodium carbonate, it undergoes a partial transformation into the anti-oxime, and the resulting mixture melts at 140—153°. When treated in ethereal solution with phosphorus pentachloride, a yellowish crust is slowly deposited, from which the ethereal solution is decanted, shaken with water and then with soda, the resulting precipitate being added to the

above insoluble crust, and hydrolysed by means of strong hydrochloric acid. Aniline and β-pyridyl phenyl ketone were discovered in the product, no benzoic acid being detectable; the alkaline solution was found to contain nicotinic acid. The formation of aniline and nicotinic acid serves to characterise the oxime as a syn-derivative.

When β-benzoylpicolinic acid is treated with hydroxylamine hydrochloride and soda, a *sodium* salt, $NOH{:}CPh{\cdot}C_5NH_3{\cdot}COONa$, is obtained in the form of large, shining prisms; it is decomposed by hydrochloric acid, yielding *phenylpyridoorthoxazinone*, $C_6H_4<\begin{matrix}CPh{\cdot}N\\CO\text{---}\end{matrix}>O$. The latter crystallises from alcohol, in which it is sparingly soluble, in the form of shining scales melting at 187—193°; the *hydrochloride* crystallises with difficulty. Phenylhydrazine acts on β-benzoylpicolinic acid with formation of 1:3-*diphenylquinolineazone* (or 1:3-*diphenylpyridopyradazone*), $C_6H_4<\begin{matrix}CPh{:}N\\CO\text{---}\end{matrix}>NPh$; it crystallises in yellowish, shining tablets, dissolves somewhat sparingly in boiling alcohol, is insoluble in sodium carbonate solution, and melts at 233—235°. The *hydrochloride* crystallises in thin, yellow tables, and the *nitrate* in radiate groups of flat leaflets.

A. L.

Cincholeuponic Acid. By ZDENKO H. SKRAUP (*Monatsh.*, 1896, **17**, 365—394).—When the hydrochloride of cincholeuponic acid is heated with about ten times its weight of strong sulphuric acid at 260—270° during 2 hours, it yields 4-methylpyridine (γ-picoline) and two methylpiperidinecarboxylic acids which were isolated, in the forms of a crystalline platinochloride and an aurochloride respectively. The *platinochloride*, $(C_7H_{13}NO_2)_2,H_2Pt_2Cl_6$, forms orange-yellow crystals which melt and intumesce at 200—202°, and dissolves with difficulty in water but is readily soluble in alcohol; the *aurochloride*,

$$C_7H_{13}NO_2,HAuCl_4,$$

crystallises in microscopic leaflets, dissolves readily in water and melts at 174°; these salts are derived from different acids, as the latter yields a crystalline compound when decomposed with hydrogen sulphide, whilst the former gives an amorphous substance, which, on treatment with gold chloride, forms an *aurochloride* not identical with the foregoing, and crystallising in small plates melting at 197—198°.

Cincholeuponic acid, when treated with acetic chloride, yields *acetylcincholeuponic anhydride*, $C_8H_{10}NO_3Ac$, which crystallises from a mixture of alcohol and ether in large prisms melting indefinitely at 130—131°, and is readily hydrolysed by warm water with production of *acetylcincholeuponic acid*, $C_8H_{12}NO_4Ac$. The latter forms a crystalline mass, and melts at 168°; its aqueous solution, on admixture with copper acetate, yields an intensely green *copper* salt, $C_8H_{10}AcNO_4Cu + 2H_2O$, which crystallises in microscopic aggregates.

Phosphorus pentachloride reacts with the hydrochloride of cincholeuponic acid, and the product when poured into water gives a yellow oil. The latter, on analysis, gave numbers in agreement with the formula $C_{27}H_{30}P_5Cl_{11}N_3$, but could not be purified; it is not affected by boiling baryta-water but dissolves in boiling nitric and hydrochloric acids.

Concentrated chromic acid mixture attacks cincholeuponic acid

liberating carbonic anhydride and hydrogen cyanide. Potassium permanganate also effects a partial oxidation, and the product contains *leuponic acid*, $C_7H_{11}NO_4$; the latter also occurs in the mother liquors of the crude hydrochloride of cincholeuponic acid, and is separated in the following manner. The hydrochloric acid is precipitated by the correct amount of silver oxide, and the filtrate evaporated; the crystals which separate in a few days are filtered off, and the mother liquors are twice subjected to similar treatment. In this way a quantity of a sparingly soluble powder is obtained which crystallises from hot water in irregular prisms, and melts and decomposes at 259—260°; it has the above composition, and acts as a dibasic acid. It forms a *hydrochloride*, $C_7H_{11}NO_4,HCl$, which crystallises in thick, facetted prisms, dissolves readily in water but is very sparingly soluble in strong hydrochloric acid, and melts indefinitely at 216—220°; it yields a crystalline *platinochloride* and an *aurochloride*, $C_7H_{11}NO_4,HAuCl_4 + H_2O$; the latter is sparingly soluble in cold water, and melts at 201—202°. *Potassium leuponate* crystallises in masses of microscopic leaflets.

Acetylleuponic anhydride, $C_7H_8NO_3Ac$, is prepared by the action of a large excess of acetic anhydride on leuponic acid; it dissolves readily in acetic acid, sparingly in alcohol, and forms crystalline aggregates melting indefinitely at 161°; it dissolves in warm water yielding *acetylleuponic acid*, $C_7H_{10}NO_4Ac$, which is more sparingly soluble in water than the anhydride, and melts at 204°. When hydrogen chloride is passed through an alcoholic solution of leuponic acid, crystals of the hydrochloride are at first deposited but gradually redissolve, and a product is obtained which does not crystallise but, on admixture with platinum tetrachloride, yields a sparingly soluble, anhydrous *platinochloride* $C_7H_9NO_4Et_2,H_2PtCl_6$; the production of this substance serves to prove that leuponic acid, like cincholeuponic acid, contains two carboxyl groups.

When cincholeuponic acid is heated with lime in an iron tube, and the distillate is neutralised with hydrochloric acid, extracted with ether and evaporated, the residue being extracted with alcohol, the soluble portion yields a *platinochloride*, $C_7H_{15}N,H_2PtCl_6$, which crystallises in orange-yellow, irregular prisms, melts and decomposes at 194—196°, and dissolves readily in water; its properties suggest that this compound is an acid salt of chloroplatinic acid, whilst such compounds are not formed by pyridine, piperidine or pyrollidine bases. The above ethereal extract on fractional distillation yields a liquid boiling at 150—200°; it gives the pyrroline reaction with a pine-shaving and has the chloroform-like odour of pure pyrroline; on analysis it gives numbers in agreement with a tetramethylpyrroline. It is probable, however, that such compounds are formed by a complicated series of reactions, and do not indicate that cincholeuponic acid is a derivative of pyrroline.

Ethylic cincholeuponate yields a *platinochloride*,

$$C_8H_{11}NO_4Et_2,H_2PtCl_6,$$

the author's original statement to the contrary having been due to the employment of unfavourable conditions; the substance crystallises in beautiful, anhydrous leaflets, and melts at 181°. Methylic iodide acts on the ethylic salt in presence of potassium carbonate, giving

diethylic methylcincholeuponate methiodide, $C_8H_{10}MeNO_4Et_2,MeI$, which dissolves readily in methylic alcohol, sparingly in chloroform and in 4 parts of cold water; it forms colourless crystals, melts at 176°, and sublimes if strongly heated, but the distillate is no longer crystalline; it is optically active, a $\frac{1}{2}$ per cent. solution in water at 20° in a 100 mm. tube producing a rotation $\alpha = -0·2155°$; by its interaction with silver chloride, a syrup is obtained which yields a crystalline *platinochloride* and *aurochloride*, of which the former crystallises in minute leaflets melting at 210—213°, whilst the latter separates from hot water in large, golden, irregular leaflets and melts at 80—82°. If the methiodide is heated with silver hydroxide, it undergoes partial hydrolysis, and the resulting syrup yields an *aurochloride*, $C_8H_{11}Me_2NO_4,EtAuCl_4$, which is very unstable and forms rectangular tables melting at 90—95°; the corresponding *platinochloride* melts at 197—198°. The behaviour of the foregoing compounds is similar to that of tropinic acid derivatives; the latter, however, differ in some respects, as they are decomposed by a warm solution of potassium carbonate, whilst the methiodide in question is not affected; in presence of alcohol, however, or when potassium carbonate is added to the boiling aqueous solution, hydrolysis does occur, and an isomeric *methiodide*, $C_8H_{10}MeNO_4Et_2,MeI$, rapidly separates. The new substance crystallises from water in stout prisms melting at 120°, and dissolves in less than its own weight of water; examined in a polarimeter under the above conditions its rotation is $\alpha = -0·4450°$; it is acted on by silver chloride, and the product yields a resinous *aurochloride* and a *platinochloride* crystallising in anhydrous microscopic grains which melt and decompose at 216°. When heated above its melting point, the new methiodide sets to a resin which contains a substance crystallising from water in tables and melting at 134°.

Both of the foregoing methiodides are decomposed by caustic potash, and the latter must be added to the amount required for complete hydrolysis and liberation of iodine, in order to render the solutions permanently alkaline; the product, in both cases, contains diethylic dimethydihydroxycincholeuponate. A. L.

Indolinones. By KARL BRUNNER (*Monatsh.*, 1896, **17**, 479—496. Compare Abstr., 1896, i, 169 and 625).—Five grams of isobutyrylphenylhydrazide is heated with six times its weight of lime at 230—260° during 4 hours; the mass is then mixed with excess of hydrochloric acid, boiled in order to decompose unaltered hydrazide, and distilled with steam; the distillate is extracted with ether, and the ethereal extracts shaken with soda, dried and evaporated. The residue, which consists of indolinone, gradually sets to a mass of crystals, and may be crystallised from petroleum; it melts at 47° and has all the properties of the substance obtained by the author on oxidising 1′:3′:3′-trimethylindolium hydroxide (*loc. cit.*).

Acetophenylmethylhydrazide, when treated in a similar manner, gives a small quantity of the corresponding indolinone, namely, methyloxindole.

Propionylphenylmethylhydrazide, in like fashion, affords some quantity of 1′:3′-*dimethyl-2′-indolinone*, $C_6H_4{<}{\substack{CHMe\\NMe}}{>}CO$; the latter

forms microscopic grains with hexagonal outlines, melts at 22·5—23°, and boils at 273—277° under 742 mm. pressure; it has a faint, blossom-like odour, is soluble in water only with difficulty, but dissolves readily in alcohol, ether, and cold concentrated acids, being reprecipitated, in the latter instance, on the addition of water. It reduces Fehling's solution after continued heating, ammoniacal silver solution suffering reduction even in the cold. The *aurochloride*, $(C_{10}H_{11}NO)_2,HAuCl_4$, is obtained as a dark red oil which solidifies when the containing vessel is scratched. The *mercuric chloride* compound, $C_{10}H_{11}NO,HgCl_2$, is precipitated as colourless leaflets which melt at 118°. On bromination, the indolinone yields a *tribromo*-derivative, $C_{10}H_8NBr_3O$, which crystallises in aggregates of yellow needles, and melts at 160°; it is not dissolved by strong aqueous potash, but is attacked by alcoholic potash, bromine being eliminated. A. L.

Constitution of the Bases formed by the action of Alkyl Iodides on Indoles. By GIACOMO L. CIAMICIAN (*Ber.*, 1896, **29**, 2460—2465).—In the following abstracts it is shown that the difference between synthetical 2′:4′-dimethyltetrahydroquinoline and the isomeric base obtained by the action of methylic iodide on indole or indoles containing methyl groups in the pyridine ring is more than one of stereoisomerism, for the two substances react differently with mercuric acetate; probably the base from indole has its two methyl groups attached to the 4′ carbon atom. Further, although synthetical trimethyldihydroquinoline and the base from indole isomeric with 1′:2′:4′-trimethyltetrahydroquinoline are oxidised to the same product, yet this synthetical trimethyltetrahydroquinoline itself is not so oxidised; consequently the isomeric base from indole must have a different constitution, probably $C_6H_4{<}\begin{matrix}CMe_2\cdot CH_2\\ \mid \\ NMe\cdot CH_2\end{matrix}$, in which case the trimethyldihydro-base would have a double bond in the 2′-3′ position. This view of their constitution is in harmony with the fact that two methyl groups can be introduced into the trimethyldihydro-base, and into an homologous dimethylethyldihydro-base. C. F. B.

Trimethyldihydroquinoline. By GIACOMO L. CIAMICIAN and ANTONIO PICCININI (*Ber.*, 1896, **29**, 2465—2471. Compare preceding abstract).—Synthetical 2′:4′-dimethyltetrahydroquinoline is oxidised to 2′:4′-dimethylquinoline by heating it for 6 hours at 150° with a 50 per cent. aqueous solution of mercuric acetate; the isomeric base from indole is not so oxidised.

Trimethyldihydroquinoline, when oxidised with alkaline permanganate or a chromic acid mixture, yields Brunner's trimethylindolinone (Abstr., 1896, i, 625), and so does the base from indole isomeric with the substance next described. 1′:2′:4′-*Trimethyltetrahydroquinoline* itself is not so oxidised, however; it was prepared by digesting 2′:4′-dimethyltetrahydroquinoline with methylic iodide at 100°; it boils at about 250° under 759 mm. pressure, and its yellow *picrate* melts at 126—127°.

Brunner's trimethylindolium hydroxide (*loc. cit.*), which may equally well be formulated as a secondary alcohol, can be reduced by heating

it at 150° with hydriodic acid and phosphorus. Some trimethylindole is formed, together with 1′:3′:3′-*trimethylindoline*, $C_6H_4<\genfrac{}{}{0pt}{}{CMe_2}{NMe}>CH_2$; the latter boils at 224—227°; its *hydriodide* melts at 184—185°, and its deliquescent *hydrochloride* at 175°, whilst its *methiodide* volatilises at 204—205°. When it is heated in an oil-bath at 215—230° with hydriodic acid and ammonium iodide, it yields 3′:3′-*dimethylindoline*, which boils at 224—230° under 758 mm. pressure, and yields a pale yellow *platinochloride* melting and decomposing at about 217°. This secondary base is not affected by heating with mercuric acetate, but distillation of its hydrochloride over zinc dust yields 2′:3′-dimethylindole and (probably) 2′-methylquinoline; in these respects it resembles the base from indole isomeric with 2′:4′-dimethyltetrahydroquinoline.

C. F. B.

Relation of Trimethylindole to Alkyldihydroquinolines. By Giacomo L. Ciamician and G. Boeris (*Ber*, 1896, **29**, 2472—2475. Compare Abstr., 1895, i, 111, 392, and preceding abstracts).—In addition to the products already obtained by distilling trimethyldihydroquinoline hydriodide, the tertiary ammonium iodide of the base from indole, 1′:4′:4′-trimethyltetrahydroquinoline, has now been isolated; the yellow *platinochloride* of this base melts and decomposes at about 208°.

When trimethylindole is treated at 110° with methylic iodide and methylic alcohol, it yields a colourless base, $C_{13}NH_{17}$, which reddens in the air and boils at 128—130° under 21 mm. pressure; its *hydriodide* melts and decomposes at 229°, and yields an indole derivative when distilled; the base itself is homologous with ordinary trimethyldihydroquinoline.

C. F. B.

Action of Ethylic Iodide on 2′-Methylindole. By Giacomo L. Ciamician and Giuseppe Plancher, and in part G. Boeris (*Ber*., 1896, **29**, 2475—2482. Compare E. Fischer and Steche, Abstr., 1888, 298). —When 2′-methylindole is heated with ethylic iodide and ethylic alcohol for 15 hours at 95—98°, the product contains two bases, the one being the ethyl derivative of the other. These bases were separated from indoles simultaneously formed by dissolving them out with hydrochloric acid; they were converted into acetyl derivatives by boiling with acetic anhydride and sodium acetate, the acetates were separated by fractionation under diminished pressure, and were then decomposed by hydrolysis, in the one case with 20 per cent. alcoholic potash, in the other (that of the ethyl derivative) by boiling with 10 per cent. hydrochloric acid.

The first base, $C_{13}H_{17}N$, is a secondary base already obtained by Fischer and Steche. It boils at 139—140° under 25 mm. pressure, and its yellow *picrate* melts at 189—190°; the *acetyl* derivative is liquid; its *benzoyl* derivative melts at 74—75°, and its compounds with *methylic* and *ethylic iodides* at 189° and 145—146° respectively. The last two are the hydriodides of tertiary bases; the ethyl compound is identical with the hydriodide of the second base obtained by the direct ethylation of 2′- methylindole; the methyl-compound crystallises in

rhombic tetrahedra; $a:b:c = 0\cdot9930:1:0\cdot9089$. The base itself, in boiling alcoholic solution, is reduced by sodium to a base $C_{13}H_{19}N$; the *hydrochloride* of this base melts at 217° and crystallises in monoclinic plates; $a:b:c = 1\cdot3314:1:1\cdot2841$; $\beta = 86°55'$. The *picrate* melts at 138° and crystallises in the triclinic system ($a:b:c = 1\cdot9727:1:1\cdot4134$; $\alpha = 113°\ 36'$; $\beta = 111°\ 30'$; $\gamma = 63°\ 18'$); and the *phenylcarbamide* melts at 149—150°; methylic iodide converts it successively into the compounds $C_{13}H_{18}NMe,HI$ and $C_{13}H_{18}NMe, MeI$, which both melt at 192°, the latter decomposing at the same time.

The second base, $C_{13}H_{16}NEt$, is a colourless oil which boils at 138—140° under 18 mm. pressure, and turns red on exposure to the air; the *hydriodide* is identical with the compound of ethylic iodide with the base $C_{13}H_{17}N$; the *acetyl* derivative crystallises in triclinic prisms or tablets ($a:b:c = 1\cdot4653:1:1\cdot6070$; $\alpha = 84°\ 49'$; $\beta = 100°\ 4'$; $\gamma = 86°\ 4'$), melts at 116—117°, and yields a yellow *platinochloride* which melts at about 200°; the *benzoyl* derivative melts at 125—126°; reduction with sodium in alcoholic solution converts the base itsel into an oily base, $C_{13}H_{18}NEt$, the yellow *picrate* of which melts at 117—119°.

C. F. B.

Action of Sulphur Haloids on Aromatic Amines. By ALBERT EDINGER (*Ber.*, 1896, **29**, 2456—2460. Compare Abstr., 1895, i, 300). —When quinoline is heated with sulphur dichloride, SCl_2, in a sealed tube at 160°, and the product boiled with dilute hydrochloric acid, a *trichloroquinoline*, devoid of basic properties, remains undissolved; it melts at 185—186°.

When the acid solution is nearly neutralised, *3′-chloroquinoline* separates; this is an oil boiling at 255° under 743 mm. pressure; the *hydrochloride* sublimes undecomposed, but melts with intumescence at 210°; the *platinochloride*, with $2H_2O$, melts above 300°; the *sulphate* at 250°, and the reddish-yellow *dichromate* at 119°; the *methiodide* sublimes at 276°. The base itself is oxidised by nitric acid to a chloropyridinemonocarboxylic acid.

When excess of alkali is added to the solution from which the chloroquinoline has been separated, a crystalline substance, *thioquinanthrene*, C_9NH_5S, is obtained; this melts with partial sublimation at 306°, and sublimes at 170° under 28 mm. pressure. It is a feebly basic substance, yielding a yellow *sulphate* which crystallises with $2H_2O$, and a dark-red *methiodide*, also with $2H_2O$, that melts above 360°; when heated with nitric acid in a sealed tube, it appears to yield a mixture of nicotinic acid with a little of a pyridinedicarboxylic acid, and hence, probably, contains the sulphur in the benzene ring. The yields of the three substances are respectively 10, 20, and 40 per cent. The sulphur base is also formed, to the extent of 30—35 per cent., when quinoline is heated with sulphur chloride, S_2Cl_2.

When sulphur bromide, S_2Br_2, is slowly added to quinoline, a reaction occurs; no sulphur base is formed, but a little *tribromoquinoline*, melting at 166°, is obtained, together with the 3′-bromoquinoline of Claus and Collischonn, which is more conveniently prepared by the present method.

C. F. B.

γ-Acetoacetylquinolyl. [4'-Acetoacetylquinoline]. By HUGO WEIDEL (*Monatsh.*, 1896, 17, 401—420).—*4'-Acetoacetylquinoline*, $C_9NH_6\cdot CO\cdot CH_2,COMe$, is obtained when ethylic cinchonate and acetone are dissolved in anhydrous benzene and treated with sodium ethoxide, the action being completed by warming at 50—60° for a few hours. It forms slender, silky needles, melts at 64—65°, boils at 205—207° (17 mm. pressure), dissolves sparingly in water, but is readily soluble in alcohol, ether, benzene, and in dilute acids or alkalis. Its solution in dilute potash gives an intense blood-red coloration with excess of ferric chloride. The *hydrochloride*,

$$C_{13}H_{11}NO_2,HCl,$$

forms fine, silky, sulphur-yellow needles, and melts at 180—181° (uncorr.); the *oxalate*, $C_{13}H_{11}NO_2,C_2H_2O_4$, crystallises in pale yellow needles, melting at 166—167°; the *platinochloride*,

$$(C_{13}H_{11}NO_6)_2,H_2PtCl_4,$$

forms small, orange-yellow needles, and melts at 192—193°. The *methiodide*, $C_{13}H_{11}NO_2,MeI, + H_2O$, forms large, lustrous, reddish-yellow ortho-rhombic needles, showing pinacoïd faces, and melts at 189—191°. The substance yields compounds with metals, that with *sodium*, $C_{10}H_{10}NaNO_2$, forming small, yellow needles. The latter substance' or even a solution of acetoacetylquinoline in strong potash, decomposes when heated with alkalis with production of acetone and cinchoninic acid.

3-Quinolyl-1-phenyl-5-methylpyrazole, $C_9NH_6\cdot C\begin{matrix} \diagup CH\text{:}CMe \\ \diagdown N—NPh \end{matrix}$, is formed when the hydrochlorides of phenylhydrazine and 4'-acetoacetylquinoline are dissolved in water and mixed with sodium acetate; it is practically insoluble in water, but dissolves readily in alcohol, ether, benzene, and light petroleum, and melts at 120°. The crystals are monoclinic, possibly hemihedral; $a:b:c = 0.6171:1:0.5319$; $\beta = 85° \ 28'$. Hydroxylamine does not yield an isoxazole with γ-acetoacetylquinoline as it does with most β-diketones, but produces the *monoxime*, $C_{13}H_{12}N_2O_2$; this crystallises in lustrous, colourless, triclinic pyramids ($a:b:c = 1.1295:1:0.9113$; $\alpha = 90° \ 50'$, $\beta = 78° \ 16'$, $\gamma = 88° \ 49'$), melts at 170–171°, is nearly insoluble in water, ether, and benzene, but dissolves readily in hot alcohol, and is rapidly attacked by ammonia and amines.

Amidoacetoacetylquinoline, $C_9NH_6\cdot CO\cdot CH\text{:}CMe\cdot NH_2$, formed by the action of anhydrous ammonia on the diketone, forms yellowish, monoclinic (?) crystals, melting at 184° (uncorr.), may be heated considerably without undergoing decomposition, and forms salts with various acids. *Anilidoacetoacetylquinoline*, $C_9NH_6\cdot CO\cdot CH\text{:}CMe\cdot NHPh$, crystallises from benzene in shining, lemon-yellow needles melting at 129·5°, dissolves readily in alcohol and benzene, and sparingly in petroleum and ether; when warmed with dilute hydrochloric acid, it is partially decomposed into its components, but the *hydrochloride*,

$$C_{19}H_{16}N_2O,2HCl,$$

may sometimes be obtained; it forms slender, red needles, and is incompletely dissolved by water owing to partial dissociation.

When γ-acetoacetylquinoline and orthoamidobenzaldehyde are warmed with the calculated quantity of alcoholic soda, 1 molecule of the former condenses with 2 of the latter with production of a new compound for which the author proposes the name *a-diquinolylquinoline*, $C_9NH_5(C_9NH_6)_2$ (compare Friedländer and Eliasberg, Abstr., 1892, i, 1107). It forms long, asbestos-like needles, dissolves readily in benzene, acetic acid, and alcohol, and melts at 150—151° (uncorr.), and is volatile at higher temperatures; the *hydrochloride*, $C_{27}H_{17}N_3,3HCl$, crystallises in dull, yellowish needles, and is partially decomposed by water and by a temperature of 100°. The *platinochloride*,

$$2(C_{27}H_{17}N_3),3H_2PtCl_4,$$

crystallises in bright-yellow, monoclinic needles, and decomposes, without melting above 200°. The *aurochloride*, $C_{27}H_{17}N_3,3HAuCl_4$, forms beautiful, glistening needles, melts with effervescence at 255°, and is decomposed by water or dilute hydrochloric acid. The *methiodide*, $C_{27}H_{17}N_3,3MeI + 2H_2O$, forms dark-red needles, and melts at 201° (uncorr.). The mother liquors from the α-diquinolylquinolin smell strongly of quinoline and, on distillation with steam, yield an oil boiling at 242°, and having all the properties of quinaldine, $C_{10}H_9N$; the production of the latter is doubtless due to the initial decomposition of the acetoacetylquinoline employed into cinchoninic acid and acetone.

A. L.

Hexahydroquinolinic Acids. By EMIL BESTHORN (*Ber.*, 1896, 29, 2662—2666. Compare Abstr., 1896, i, 252).—The author has described (*loc. cit.*) the preparation of two isomeric acids obtained by the reduction of quinolinic acid. The higher-melting, more sparingly-soluble one he assumes to be the *trans*-modification, the second substance being therefore the *cis*-form.

The nitroso-derivative of the *cis*-modification may be made to assume a solid form under suitable conditions; it melts and decomposes at 138—139°. It forms a well-defined strychnine salt, by means of which it may be partially resolved into its optically active components. When the acid in a solution having a distinct rotatory power is converted into the corresponding hexahydroquinolinic acid, all measurable activity is found to have disappeared, but may be brought back by the addition of nitrite to the acidified solution. The melting point of the most active nitroso-acid obtained was 152—153°, or 14° above that of the racemic modification. The partly resolved hexahydroquinolinic acids, when observed in convergent polarised light, were found to exhibit ring-systems unnoticeable in the racemic acid.

Dry bromine is without action on the hydrochloride of the *cis*-acid at 150°; in presence of water, however, action takes place to some extent even at 100°, carbonic anhydride being evolved. The product is readily soluble in water, and melts at 112°, subliming slowly at 100° in beautiful, white needles. Its solubility at 100° precludes the possibility of its identity with $\beta\beta$-dibromopyridine, with which it agrees in melting point and volatility.

A. L.

Derivatives of Isocoumarin, Isocarbostyril, and Isoquinoline. By CHARLES A. HARPER (*Ber.*, 1896, 29, 2543—2549).—Orthocyanobenzylic cyanide prepared by the method of Gabriel and Otto, from orthocyanobenzylic chloride and potassium cyanide, condenses with metanitrobenzoic chloride in the presence of sodium hydroxide, and on subsequently acidifying the mixture the condensation product. *4-cyano-3-metanitrophenylisocoumarin*, $C_6H_4<\begin{matrix}C(CN):C\cdot C_6H_4\cdot NO_2, \\ CO\text{——}O\end{matrix}$ is precipitated as a dark brown powder. It crystallises from glacial acetic acid as a yellow-crystalline powder melting at 210—211°, and is insoluble in ether and light petroleum.

3-Metanitrophenylisocoumarin, $C_6H_4<\begin{matrix}CH:C\cdot C_6H_4\cdot NO_2, \\ CO\cdot O\end{matrix}$ is formed on heating the cyano-compound with a mixture of glacial acetic and concentrated hydrochloric acids (1 : 2) in a sealed tube for 2 hours at 180°, and pouring the mixture into water. It melts at 232—233° after recrystallisation from glacial acetic acid.

4-Cyano-3-metanitrophenylisocarbostyril, $C_6H_4<\begin{matrix}C(CN):C\cdot C_6H_4\cdot NO_2, \\ CO\text{——}NH\end{matrix}$ is formed when the corresponding isocoumarin is heated in a closed tube for 12 hours at 100° with 20 parts of an alcoholic solution of ammonia; this is insoluble in alcohol and ether, melts above 315°, and is not acted on by phosphorous oxychloride. When heated in a closed tube for 1½ hour at 180° with acetic and hydrochloric acids, *3-metanitrophenylisocarbostyril* melting at 298—300° is produced; this is readily converted, by heating for 15 minutes on the water bath with phosphorous oxychloride, into *1-chloro-3-metanitrophenylisoquinoline*,

$$C_6H_4<\begin{matrix}CH:C\cdot C_6H_4\cdot NO_2 \\ CCl:N\end{matrix};$$

the latter crystallises in long, white needles, melting at 220—223°, and is insoluble in ether, cold alcohol, nitrobenzene, and glacial acetic acid.

4-Cyano-3-paratolylisocoumarin, $C_6H_4<\begin{matrix}C(CN):C\cdot C_6H_4Me, \\ O\text{——}O\end{matrix}$ is obtained on condensing orthocyanobenzylic cyanide with paratoluic chloride under the same conditions, the best yield being obtained when small quantities are worked with; it is a yellow powder melting at 193—195°.

α-Orthodicyano-β-acetoxyparamethylstilbene,

$$CN\cdot C_6H_4\cdot C(CN):C(OAc)\cdot C_6H_4Me,$$

is obtained as an intermediate product in this condensation; it crystallises in rhombic prisms melting at 186—188°.

Paramethyldeoxybenzoinorthocarboxylic acid,

$$C_6H_4Me\cdot CO\cdot CH_2\cdot C_6H_4\cdot COOH,$$

is formed on heating 4-cyano-3-paratolylisocoumarin with glacial acetic and hydrochloric acids in a closed tube at 160°, and melts at 147—148°. It is identical with the compound obtained by Ruhemann from nitroparaxylylidenephthalide.

3-Paratolylisocarbostyril, also previously prepared, is formed when

4-cyano-3-paratolylisocoumarin is heated with ammonia or by hydrolysing *4-cyano-3-paratolylisocarbostyril*, $C_6H_4<\begin{matrix}C(CN){:}C\cdot C_6H_4Me \\ CO\text{---}NH\end{matrix}$, with concentrated hydrochloric and acetic acids, and subsequently eliminating carbonic anhydride. The carbostyril compound is readily formed from the isocoumarin compound on treating it with an alcoholic solution of ammonia. It crystallises in yellow needles and melts at 290—292°.

J. F. T.

Action of Sulphuryl Chloride on Carbazole: Mono- and Di-Chlorocarbazoles. By GIROLAMO MAZZARA and MANFREDO LAMBERTI-ZANARDI (*Gazzetta*, 1896, **26**, ii, 236—242).—*Monochlorocarbazole*, $C_{12}NH_8Cl$, is prepared by heating a chloroform solution of carbazole on the water bath with sulphuryl chloride; after distilling off the solvent and recrystallising, it is obtained in lustrous, white scales, melting at 192—193°. Its *acetyl*-derivative, $C_{12}H_7ClNAc$, prepared by heating it with acetic anhydride in a sealed tube at 180—200°, crystallises in dull, white needles melting at 124—125°.

Dichlorocarbazole, $C_{12}NH_7Cl_2$, is prepared similarly, and crystallises in white pyramids melting at 202—203°; its *acetyl*-derivative crystallises in opaque, white needles, melting at 185—186°.

Benzoylcarbazole is not chlorinated on heating it with sulphuryl chloride in chloroform solution.

W. J. P.

Conversion of Phenosafranine and Rosinduline into the corresponding Azonium Compounds. By FRIEDRICH KEHRMANN (*Ber.*, 1896, **29**, 2316—2322).—Further facts are brought forward tending to prove the correctness of the author's theory (*Annalen*, 1896, **290**, 256) of the constitution of the safranines. It is now found that both aposafranine and rosinduline can be readily diazotised, provided the solution be sufficiently strongly acid, and by decomposing these diazo-compounds with alcohol the corresponding azonium bases are produced: in the former case, phenazonium, and in the latter naphthophenazonium.

The method employed is to dissolve aposafranine chloride in a small quantity of water and add first strong sulphuric acid until the colour becomes green, and then a solution of sodium nitrite until it changes to orange-red. Absolute alcohol is then added, and the reaction allowed to proceed 6 hours, after which time the conversion of the diazo-sulphate into phenazonium sulphate is complete. From this, the compound with ferric chloride is precipitated by means of ferric chloride, and recrystallised from glacial acetic acid, from which it separates in fine, red-brown prisms. On adding ammonium carbonate to a solution of this iron salt, iron oxide is precipitated, and the azonium carbonate remains in solution. This solution is rapidly decomposed by ammonia; with sodium hydroxide, aposafranone is produced, and with dimethylaniline, the violet dimethylaposafranine. Strong sulphuric acid dissolves the chloride with the production of a colour similar to that of acetylaposafranine.

Naphthophenazonium is produced in precisely the same way from rosinduline; the compound with ferric chloride crystallises from glacial

acetic acid in glistening, metallic green plates which appear red by transmitted light. The solutions of naphthophenazonium show the same coloration as the salts of acetylrosinduline, the colour of the sulphuric acid solutions of the two substances being also similar.

From these facts the author considers that there can no longer be any doubt that both acetylaposafranine and acetylrosinduline are azonium compounds.

Similarly, phenylisonaphthophenazonium prepared from β-naphthaquinone and phenylorthophenylenediamine gives on solution in concentrated sulphuric acid, a coloration similar to that of acetylisorosinduline. The compound of phenylisonaphthophenazonium with ferric chloride crystallises in glistening, golden leaves. J. F. T.

Constitution of the Safranines. By RUDOLF NIETZKI (*Ber.*, 1896, **29**, 2771—2773. Compare Otto Fischer, Abstr., 1896, i, 628).—The author defends his adherence to the azonium theory of the constitution of the safranines, and criticises the objections of Fischer (*loc. cit.*). M. O. F.

Configuration of Quinone-imide Dyes. By WILHELM VAUBEL (*J. pr. Chem.*, 1896, [2], **54**, 292—304).—The author reviews the theories which have been put forward with regard to the constitution of the dyes of this class, and shows how his configuration for benzene (Abstr., 1894, i, 325) will serve to explain such cases of isomerism as may exist in the class. A. G. B.

Behaviour of Quinone-imide Dyes toward nascent Bromine. By WILHELM VAUBEL (*J. pr. Chem.*, 1896, [2], **54**, 289—291. Compare Abstr., 1895, i, 55).—Phenosafranine combines with 4 atoms of bromine; indazine with 1 atom, rosinduline and rosindone with 1 atom. Meldola's blue readily combines with bromine; methylene blue combines with 1 atom and resorufin with 4 atoms of bromine. A. G. B.

Behaviour of Antipyrine towards Alkyl Haloids. By LUDWIG KNORR (*Annalen*, 1896, **293**, 1—41).—Soon after the discovery of antipyrine, the action of methylic iodide on it at high temperatures was studied, but, instead of the methiodide of the base, a mixture of 1-phenyl-2:3:4-trimethyl-5-pyrazolone (4-methylantipyrine) and 1-phenyl-3:4:4-trimethyl-5-pyrazolone was produced. It is now found that at ordinary temperatures, on application of a moderate heat (60°), antipyrine combines with ethylic iodide, forming a quaternary iodide, isomeric with the methiodide of 1:3:2-phenylmethylethyl-5-pyrazolone (homoantipyrine); the substance, therefore, is not a true ethiodide of antipyrine, being identical with the methiodide derived from the ethyl ether of 3:1-methylphenyl-5-pyrazolone. In view of this fact, the author refers to the new class of compounds as *antipyrine pseudo-alkyliodides*, and expresses the change which results in their production by the equation,

$$\left.\begin{matrix}\mathrm{NR'\cdot CMe} \\ | \\ \mathrm{NPh\cdot CO}\end{matrix}\right\rangle \mathrm{CH} + \mathrm{R''I} = \left.\begin{matrix}\mathrm{I\cdot NR' = CMe} \\ | \\ \mathrm{NPh\cdot C(OR'')}\end{matrix}\right\rangle \mathrm{CH}.$$

This group of quaternary iodides differs from other quaternary iodides in behaviour towards alkalis and also on fusion, antipyrine being regenerated in each case.

As already stated, the action of methylic iodide on antipyrine at temperatures between 80° and 200° gives rise to a mixture of 4-methylantipyrine and 1-phenyl-3:4:4-trimethyl-5-pyrazolone; these substances are produced in varying quantities according to the conditions observed, a table in the original paper recording the author's results in this direction. It is, moreover, shown that the conversion of the former subtance, which constitutes the primary product of action, into 1-phenyl-3:4:4-trimethyl-5-pyrazolone, does not depend on molecular rearrangement, but arises from the further action of methylic iodide.

5:1:3-*Methoxyphenylmethylpyrazole methiodide* (*antipyrine pseudo-methiodide*), $\begin{matrix} \text{I·NMe} = \text{CMe} \\ \mid \\ \text{NPh·C(OMe)} \end{matrix}\!\!>\!\text{CH}$, is obtained when antipyrine or 5:1:3-methoxyphenylmethylpyrazole (Abstr., 1895, i, 397) remains with excess of methylic iodide in closed vessels for several days at 60°; it decomposes and melts somewhat indefinitely at 130°, yielding antipyrine and methylic iodide. It separates from a mixture of ether and alcohol in crystals which belong to the monoclinic system, and has a sp. gr. = 1·580 at 22°. The *platinochloride* of the methochloride crystallises in orange needles, and decomposes about 210°.

5:1:3-*Ethoxyphenylmethylpyrazole methiodide* (*antipyrine pseudo-ethiodide*), $\begin{matrix} \text{I·NMe} = \text{CMe} \\ \mid \\ \text{NPh·C(OEt)} \end{matrix}\!\!>\!\text{CH}$, is obtained from antipyrine and ethylic iodide, or from 3:1-methylphenyl-5-ethoxypyrazolone and methylic iodide; it forms monoclinic crystals having a sp. gr. = 1·583 at 17·5°, and melts and decomposes at 113—116°, yielding antipyrine and ethylic iodide. The *platinochloride* of the corresponding methochloride melts and decomposes at about 198°.

5:1:3-*Methoxyphenylmethylpyrazole ethiodide* (*homoantipyrine-pseudo-methiodide*), $\begin{matrix} \text{I·NEt} = \text{CMe} \\ \mid \\ \text{NPh·C(OMe)} \end{matrix}\!\!>\!\text{CH}$, is obtained from the higher homologue of antipyrine, 1:3:2-phenylmethylethyl-5-pyrazolone and methylic iodide; it melts at 114—115°, and yields methylic iodide and homoantipyrine. Boiling caustic soda also regenerates homoantipyrine, which distinguishes the original substance from the isomeric antipyrine pseudo-ethiodide. The *platinochloride* of the corresponding ethochloride crystallises in orange prisms, and decomposes at about 195°.

5-*Hydroxyethoxy*-1:3-*phenylmethylpyrazole methiodide*,

$$\begin{matrix} \text{I.NMe} = \!=\!=\!= \text{CMe} \\ \mid \\ \text{NPh·C(O·C}_2\text{H}_4\text{·OH)} \end{matrix}\!\!>\!\text{CH},$$

is prepared from 5-hydroxyethoxy-1:3-phenylmethylpyrazole (*loc. cit.*), and melts at 129—130°. The *platinochloride* of the methochloride crystallises in orange prisms, and melts at 202°.

The unexpected result of treating antipyrine with methylic iodide

at common temperatures recalls the behaviour of phenolbetaïnes towards this agent; thus trimethylphenolammonium, $C_6H_4<\begin{array}{c}O\\ |\\ N\end{array}Me_3$, described by Griess (*Ber.*, 13, 246), yields with potash and methylic iodide trimethylanisoïlammonium iodide, $OMe\cdot C_6H_4\cdot NMe_3I$, which is derivable, under the same conditions, from dimethylamidoanisoïl,

$$OMe\cdot C_6H_4\cdot NMe_2.$$

This similarity of behaviour suggests a phenolbetaïne formula for antipyrine, but on comparing the substance more closely with the betaïne of orthohydroxyphenyltrimethylammonium hydroxide it is found that the analogy is not sustained, for whilst the latter compound has an alkaline action in aqueous solution, and is not precipitated by alkalis, antipyrine is neutral, and separates from its solution on the addition of alkalis; moreover, orthohydroxyphenyltrimethylammonium hydroxide is converted into orthodimethylamidoanisoïl when distilled, antipyrine undergoing this treatment without change. Characteristic differences also present themselves when the alkylic iodide additive products of both compounds are submitted to comparison.

Some interesting observations are made regarding the theoretical aspect of these results, and the author points out that the phenomena described may be traced to the nitrogen atom 2, which is alternatively ter- and quinque-valent, whilst the behaviour of antipyrine is best explained on the hypothesis that it assumes one of the four modifications,

$$\text{I}\quad \begin{array}{l}-NMe{:}CMe—\\ \;|\\ NPh—C(O\cdot)\end{array}{>}CH \qquad \text{II}\quad \begin{array}{l}{=}NMe\cdot CMe\\ \;|\\ NPh—CO\end{array}{>}CH$$

$$\text{III}\quad \begin{array}{l}-NMe{:}CMe\\ \;|\\ NPh—CO\end{array}{>}CH- \qquad \text{IV}\quad \begin{array}{l}NMe\cdot CMe—\\ \;|\\ NPh—CO\end{array}{>}CH-$$

according to the circumstances in which it is placed. This view finds support in the behaviour of the substance towards bromine (Abstr., 1887, 603), which occupies the positions 3:4. Towards methylic iodide, at temperatures above 80°, antipyrine behaves as a compound having the structure represented by II and III, whilst the form I is assumed when the substance is treated with methylic iodide at the ordinary temperature. M. O. F.

Additive Product of Antipyrine and Benzoic Chloride. By Ludwig Knorr and Paul Rabe (*Annalen*, 1896, **293**, 42—48).—In accordance with the unsaturated character of antipyrine (compare foregoing abstract), the substance forms an additive product with benzoic chloride, but it is not decided at present whether the benzoyl group is attached to oxygen or nitrogen.

Antipyrine benzochloride,

$$\begin{array}{l}Cl\cdot NMeBz\cdot CMe\\ \quad|\\ \;NPh——CO\end{array}{>}CH \text{ or } \begin{array}{l}Cl\cdot NMe{=}CMe\\ \quad|\\ \;NPh\cdot C(OBz)\end{array}{>}CH,$$

is obtained on adding freshly distilled benzoic chloride (140 parts) to

antipyrine (188 parts) dissolved in benzene (2,000 parts); it is readily soluble in water, alcohol, acetone, and chloroform, and insoluble in ether, petroleum, and benzene. The substance crystallises slowly in prisms on adding benzene to the solution in chloroform, and melts at 129—130°, forming a colourless liquid, which becomes red and evolves gas at 180°. The benzochloride is much more sensitive towards alkalis than the pseudo-alkyliodides, and is also slowly decomposed by cold water, yielding antipyrine, whilst the pseudo-alkyliodides are indifferent towards boiling water.

When heated at 180°, antipyrine benzochloride gives rise to benzoic and methylic chlorides, antipyrine, and Nef's benzoylphenylmethyl-5-pyrazolone, which melts at 75° (Abstr., 1892, 146); only one third of the original substance, however, breaks up in such a manner as to yield methylic chloride and benzoylphenylmethylpyrazolone. The corresponding benzoiodide, which according to Stolz (private communication) is obtained by the action of methylic iodide on benzoylphenylmethylpyrazolone dissolved in benzene, yields the last-named substance in quantity amounting to 75 per cent. when heated; its identity with Nef's compound is established by the production, from both preparations, of the same *picrate*, which melts at 119—120°, and has a sp. gr. = 1·42 at 12°.

According to these results, the benzoyl group occupies the same position in antipyrine benzochloride as in benzoylphenylmethylpyrazolone; if Nef's formula for the latter substance, $\begin{array}{l}\mathrm{NBz\cdot CMe}\\ \mid \\ \mathrm{NPh\cdot CO}\end{array}\!\!>\!\mathrm{CH}$, is correct, the addition of benzoic chloride to antipyrine proceeds in a sense different from the addition of alkylic iodides, a course which the author considers improbable. M. O. F.

4-Hydroxy-1-phenyl-2 : 3-dimethyl-5-pyrazolone (4-hydroxyantipyrine). By LUDWIG KNORR and ROBERT PSCHORR (*Annalen*, 1896, **293**, 49—55).—4-*Hydroxyantipyrine*, $\begin{array}{l}\mathrm{NMe\cdot CMe}\\ \mid \\ \mathrm{NPh{-\!\!-}CO}\end{array}\!\!>\!\mathrm{C\cdot OH}$, is obtained by heating equal quantities of 4-hydroxy-1 : 3-phenylmethyl-5-pyrazolone and methylic iodide with methylic alcohol for 8 hours at 110°, and treating the product with sulphurous acid; it is also formed when 4-bromantipyrine is treated with excess of hot, concentrated potash. The substance is readily soluble in alcohol, chloroform, benzene, and hot water, but only sparingly so in ether and petroleum; it crystallises in colourless needles, and melts at 182°. Hydroxyantipyrine is phenolic in character, and the *sodium* derivative is decomposed by carbonic anhydride. The *methyl ether* crystallises from ether and light petroleum in small plates, and melts at 75°; the *ethyl ether* crystallises from petroleum of high boiling point in small needles, and melts at 60°. The *benzoate* crystallises from toluene and melts at 139°.

4-Hydroxyantipyrine *dibromide*, $\begin{array}{l}\mathrm{NMe\cdot CBrMe}\\ \mid \\ \mathrm{NPh{-\!\!-\!\!-}CO}\end{array}\!\!>\!\mathrm{CBr\cdot OH}$, separates in colourless needles from the chloroform solution on the addition of ether,

and melts at 218—220°; the action of water regenerates hydroxyantipyrine. M. O. F.

Reduction of Nitroso-antipyrine. By Ludwig Knorr and Theodor Geuther (*Annalen*, 1896, **293**, 55—57).—4-Amido-antipyrine *hydrochloride* is obtained by reducing nitroso-antipyrine or nitro-antipyrine (Abstr., 1892, 730); it forms colourless crystals, and melts, decomposing, at 231°. The *platinochloride* forms bright yellow crystals.

Antipyrine-azo-β-naphthol is produced when an alkaline solution of β-naphthol is added to diazotised amido-antipyrine, and crystallises from glacial acetic acid in red needles.

Nitroso-antipyrine *hydrochloride* crystallises in small, yellow needles, and melts and decomposes at 80°; it is an unstable substance, gradually losing hydrogen chloride when exposed to air; water reconverts it into nitroso-antipyrine. M. O. F.

4-Amidoantipyrine. By Ludwig Knorr and Friedrich Stolz (*Annalen*, 1896, **293**, 58—69).—The method described in the foregoing abstract is not suited for the production of 4-amidoantipyrine in considerable quantity; it is most conveniently prepared by reducing nitroso-antipyrine dissolved in alcohol with zinc dust and glacial acetic acid, and when the reddish-violet liquid has become pale yellow, converting the base into the benzylidene derivative by means of benzaldehyde.

4-*Amido-antipyrine*, $\begin{array}{l}NMe{\cdot}CMe\\ |\\ NPh—CO\end{array}\!\!>\!C{\cdot}NH_2$, crystallises from benzene in minute, pale yellow needles, and melts at 109°; it is sparingly soluble in ether, but dissolves readily in benzene, alcohol, and water. The *sulphate* dissolves with difficulty in alcohol, and separates from water in plates melting at 215°; the *picrate* crystallises in leaflets, and melts at 144°. The *benzylidene* derivative crystallises from alcohol in lustrous, yellow leaflets, and melts at 173°; the *hydroxybenzylidene* and *metanitrobenzylidene* derivatives melt at 194° and 213° respectively, whilst the *cinnamylidene* derivative melts at 160°. Amido-antipyrine forms a *compound*, $C_{17}H_{21}N_3O_3$, with ethylic acetoacetate, which crystallises from dilute alcohol in colourless needles, and melts at 158—160°; the *compound*, $C_{17}H_{17}N_3O_5$, obtained from amido-antipyrine and pyruvic acid, crystallises from alcohol in bright yellow, lustrous prisms, and melts at 170°. The *acetyl* derivative of amido-antipyrine crystallises from toluene, and melts at 197°, whilst the *formyl* derivative melts at 189°; the *dibenzoyl* derivative crystallises from alcohol, and melts at 188°. *Antipyrylcarbamide* crystallises in leaflets and melts at 245°, whilst *symmetrical diantipyrylthiocarbamide* melts and decomposes at 248°; the *urethane* derivative crystallises from dilute alcohol and melts at 206°.

4-*Dimethylamido-antipyrine* separates from a mixture of petroleum and ethylic acetate in colourless crystals, and melts at 108°; the *methiodide* crystallises slowly from water, and melts indefinitely at 220°.

Diazo-antipyrine chloride is obtained in solution by the action of nitrous acid on amido-antipyrine; when sodium acetate is added to a mixture of the substance with aniline acetate, *diazo-antipyrineamidobenzene* separates as a yellow precipitate, and decomposes at 136—137°. Diazo-antipyrine combines with phenols forming azo-colouring matters. The *antipyrylhydrazone* of 1:3-phenylmethyl-4:5-ketopyrazolone is obtained on adding methylphenylpyrazolone in glacial acetic acid to a solution of diazo-antipyrine chloride; it crystallises from alcohol in beautiful red needles, and decomposes at 200—205°.

M. O. F.

Pyrazolone Derivatives. By R. HIMMELBAUER (*J. pr. Chem.*, 1896, [2], 54, 177—214. Compare Abstr., 1895, i, 570.)—*Methylic 1:3-phenylmethyl-5-pyrazolone-2-carboxylate*, $\begin{matrix} CMe{\cdot}NPh \\ \| \\ CH{-\!\!-}CO \end{matrix}\!\!>\!N{\cdot}COOMe$, is prepared by dissolving the pyrazolone (1 mol.) in cold sodium hydroxide (1 mol.) solution and adding methylic chlorocarbonate (1 mol.); after 12 hours, during which time the containing vessel must be frequently shaken, the lower, oily layer is dissolved in ether, dried by lime and evaporated. The yield is 91·5 per cent. of that calculated. The compound is also formed in the absence of alkali, but a high temperature is then necessary. It forms brilliant, well-built, compact crystals, melts at 52°, and is freely soluble in all the usual solvents, except water, mineral acids, and alkalis. The ease with which the carboxymethyl group can be eliminated by hydrolysing agents is characteristic of this salt. Ferric chloride gives no coloration with the alcoholic solution of the salt, nor does nitrous acid react with it to form a nitroso-compound; with bromine, it yields an additive product. When heated at 180° and finally at 250° the methylic carboxylate loses carbonic anhydride, 1:2:3-phenyldimethyl-5-pyrazolone (antipyrine) and 1:3-phenylmethylmethoxypyrazole (Knorr, Abstr., 1895, i, 397) being formed.

Ethylic 1:3-phenylmethyl-5-pyrazolone-2-carboxylate has been already described (Abstr., 1895, i, 570); at 300° it loses carbonic anhydride and if the hot residue be added to absolute alcohol, crystals of carbo-bis-1:3-phenylmethyl-5-pyrazolone separate, on cooling (see below). The mother liquor from these crystals, when evaporated and distilled with steam, yields 1:3-phenylmethyl-5-ethoxypyrazole (Abstr., 1895, i, 396), which may be extracted by ether; the aqueous solution contains 1:2:3-phenylethylmethyl-5-pyrazolone (Aldrich, Diss. Jena, 1892, 20). The *platinochloride* (with $2H_2O$) and the *nitroso*-derivative were prepared.

Carbo-bis-1:3-phenylmethyl-5-pyrazolone,

$$NPh<\begin{matrix} N{=\!\!=}CMe \quad\quad CMe{:}N \\ \quad\;\; | \qquad\qquad\; | \\ CO{\cdot}C{=\!\!=}C{=\!\!=}C{\cdot}CO{-\!\!-} \end{matrix}>NPh,$$

is obtained as already stated, and also when carbonyl chloride is passed into melted phenylmethylpyrazolone (antipyrine) at 150—180°; the mass is powdered, washed with dilute acid, and fractionally crystallised from absolute alcohol, in which the carbo-compound is less soluble than the condensation product mentioned below. It crystallises in white,

silky needles, melts at 235° and is insoluble in dilute mineral acids and alkalis, sparingly soluble in alcohol and benzene, more freely in glacial acetic acid and phenol; it can be distilled under diminished pressure. The *condensation* product which crystallises from the mother liquor of the foregoing compound is the main product of the action; it forms brick-red crystals, does not melt at 280° and is easily soluble in alkalis and fairly soluble in hot alcohol, glacial acetic acid, phenol and strong hydrochloric acid. 1:3-Phenylmethyl-5-pyrazolone-4-acetic acid, $NPh<\begin{matrix} N{=\!=}CMe \\ \quad\;\, | \\ CO\cdot CH\cdot CH_2\cdot COOH \end{matrix}$, has been prepared by the action of ethylic acetosuccinate on phenylhydrazine (Knorr and Blank, Abstr., 1884, 1380); it is now obtained by heating phenylmethylpyrazolone, dissolved in alkali, with an equivalent of sodium chloracetate. When heated at 200°, it loses carbonic anhydride and yields 1:3:4-phenyldimethyl-5-pyrazolone (Knorr., Abstr. 1887, 601); this melts at 130°.

2:1:3-Benzoylphenylmethylpyrazolone has been described by Nef (Abstr., 1892, 146); it is debenzoylised when treated with phenylhydrazine or hydroxylamine.

1:2:3-*Phenylsulphonemethyl-5-pyrazolone*, $NPh<\begin{matrix} N(SO_2Ph)\cdot CMe \\ \qquad\qquad\;\; \| \\ CO \text{———} CH \end{matrix}$, from benzenesulphonic chloride and commercial phenylmethylpyrazolone, melts at 91—92° and dissolves freely in ether, alcohol and benzene but not in water.

1:2:3-*Phenylbenzylmethyl-5-pyrazolone* crystallises in needles, melts at 134—136° and has the same solubility as commercial pyrazolone. The substance obtained by Knorr by reducing 1:3:4-phenylmethylbenzylidenepyrazolone (Abstr., 1887, 602) has the formula $C_{21}H_{20}N_3O_2$ and melts at 157°; it is therefore not the benzyl derivative.

2:1:3-*Acetylphenylmethyl-5-pyrazolone*, from phenylmethylpyrazolone and acetic chloride in benzene solution, is a pale yellow oil, boils at 200° (10 mm.) and is insoluble in water, alkalis and acids, but soluble in the usual organic solvents. *Methylic 1:3:4-phenyldimethyl-5-pyrazolone-2-carboxylate* $NPh<\begin{matrix} N(COOMe)\cdot CMe \\ \qquad\qquad\;\; \| \\ CO \text{————} CMe \end{matrix}$, is obtained by shaking the pyrazolone with methylic chlorocarbonate in an alkaline solution; it is an oil which solidifies at low temperatures and decomposes when distilled, even in a vacuum; most solvents dissolve it, except water, acids and alkalis. The distillate from this salt yields 1:3:4-phenyldimethyl-5-methoxypyrazole (Abstr., 1895, i, 397) when distilled with steam. The original residue of the distillation also contains 1:2:3:4-phenyltrimethyl-5-pyrazolone (m. p. 82°).

1:3:4-*Phenyldimethyl-5-pyrazolone-2-acetic acid* is prepared by heating sodium chloracetate with the pyrazolone in alkaline solution for 2 minutes; it crystallises in white needles (with $1H_2O$), melts at 102°, and loses its water of crystallisation at 115°; it dissolves easily in alcohol and ether, and sparingly in boiling water. 1:3:4-*Phenyldimethyl-5-pyrazolone-4-acetic acid*, $NPh<\begin{matrix} N{=\!=}CMe \\ \quad\;\, | \\ CO\cdot CMe\cdot CH_2\cdot COOH \end{matrix}$, is formed

if the heating be continued for 25—30 minutes in a reflux apparatus; it melts at 190°. A. G. B.

Syntheses of Quinazolines. By CARL PAAL (*J. pr. Chem.*, 1896, [2], **54**, 258—264. Compare Abstr., 1894, i, 210).—An introduction to the four succeeding papers. A. G. B.

Synthesis of 3′-Orthamidophenyldihydroquinazoline. By CARL PAAL and GEO KROMSCHRÖDER (*J. pr. Chem.* 1896, [2], **54**, 265—270).—*Orthonitrobenzylorthonitraniline*, $NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}NH{\cdot}C_6H_4{\cdot}NO_2$, is prepared by heating orthonitrobenzylic chloride (1 mol.) with orthonitraniline (2 mols.) in an oil bath for 2 hours at 130°, and the cooled mass is treated with hot, dilute hydrochloric acid, when the new compound is left undissolved. It crystallises in laminæ which have a golden lustre, melts at 137°, and dissolves sparingly in alcohol, but more freely in benzene and glacial acetic acid; it has no basic properties.

Orthonitrobenzylorthophenylenediamine,

$$NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}NH{\cdot}C_6H_4{\cdot}NH_2,$$

is obtained as its hydrochloride when orthonitrobenzylic chloride (1 mol.) and orthophenylenediamine (1 mol.) are heated together in strong alcoholic solution; it crystallises in red needles, melts at 115°, and dissolves in alcohol, ether, glacial acetic acid, ethylic acetate, chloroform and benzene. The *hydrochloride*, $C_{13}H_{13}N_3O_2{,}HCl$, crystallises in white needles and melts at 202°. The *formyl*-derivative, $NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}N(C_6H_4{\cdot}NH_2){\cdot}CHO$, is formed when the phenylenediamine is heated with anhydrous formic acid; it crystallises in thick, pale yellow tablets, melts at 158°, and dissolves in most of the usual organic solvents; it is somewhat basic. A second compound obtained at the same time was found to melt at 138°, but has not been further investigated. By reduction in alcoholic solution by means of tin and hydrochloric acid, the formyl-derivative yields *3′-orthamidophenyldihydroquinazoline*, $C_6H_4{<}\begin{matrix}N{=}CH\\ \quad\;\;|\\ CH_2{\cdot}N{\cdot}C_6H_4{\cdot}NH_2\end{matrix}$; this forms pale yellow crystals, melts at 165°, dissolves in most organic solvents, save light petroleum, and is strongly basic; the *hydrochloride* is very unstable; the *picrate* (m. p. 184°) and the *oxalate* (with $2H_2O$) are described. A. G. B.

Synthesis of 3-Paramidophenyldihydroquinazoline. By CARL PAAL and H. POLLER (*J. pr. Chem.*, 1896, [2], **54**, 271—277).—*Orthonitrobenzylparanitraniline* is prepared from orthonitrobenzylic chloride and paranitraniline (compare preceding abstract); it crystallises in large laminæ, with a bronze lustre, melts at 202°, and has no basic properties. When reduced by zinc dust and glacial acetic acid at a temperature not exceeding 40°, it yields *orthamidobenzylparaphenylenediamine*, $NH_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}NH{\cdot}C_6H_4{\cdot}NH_2$, this crystallises in nearly colourless laminæ, and melts at 114°; the *hydrochloride* and the *oxalate* were obtained.

Formorthonitrobenzylparanitranilide, obtained by heating the nitrani-

line with anhydrous formic acid, crystallises in thick, short, yellowish prisms, melts at 155—156°, and dissolves sparingly in alcohol and more freely in benzene. When suspended in alcohol and heated with granulated tin in a reflux apparatus, strong hydrochloric acid being added in small portions at a time, the formyl-derivative is reduced to *3'-paramidophenyldihydroquinazoline*, which crystallises in the form of its *stannochloride*, $C_{14}H_{13}N_3,2HCl,2SnCl_2$; the double salt is decomposed in the usual manner whereby the quinazoline is obtained in flat, white, feathery needles. It melts at 175°, and is freely soluble in dilute mineral acids, alcohol and chloroform, more sparingly in ethylic acetate and benzene, and hardly at all in water and light petroleum. The *hydrochloride*, $C_{14}H_{13}N_3,2HCl,2H_2O$, *hydrobromide*, $C_{14}H_{13}N_3,2HBr$, *platinochloride*, *oxalate* (m. p. 237°), and *picrate* (m. p. 199°) are described.

3'-Paramidophenyltetrahydroquinazoline, $C_6H_4<\begin{matrix} NH\cdot CH_2 \\ \vert \\ CH_2\cdot N\cdot C_6H_4\cdot NH_2 \end{matrix}$, is produced when the dihydroquinazoline is reduced by metallic sodium in hot alcoholic solution; it crystallises in small, flat, white needles, melts at 138°, and dissolves freely in alcohol and ethylic acetate, more sparingly in ether, chloroform and benzene, but hardly at all in water or light petroleum; the solutions become violet on exposure to the air. The *hydrochloride*, *platinochloride*, *oxalate*, and *picrate* were obtained. A. G. B.

Synthesis of 3'-Orthanisyldihydroquinazoline. By CARL PAAL and WILHELM SCHILLING (*J. pr. Chem.*, 1896, [2], **54**, 277—283).—*Orthonitrobenzylorthanisidine*, $NO_2\cdot C_6H_4\cdot CH_2\cdot NH\cdot C_6H_4\cdot OMe$.—When orthonitrobenzylic chloride (1 mol.) and orthanisidine (2 mols.) are heated together in alcoholic solution which is afterwards mixed with sodium acetate and acetic acid, diluted with water and extracted by ether, two compounds are obtained; they are separated by dissolving in alcohol the residue left on evaporation of the ether and adding alcoholic hydrogen chloride and ether, whereby white needles of orthonitrobenzylorthanisidine *hydrochloride*, $C_{14}H_{14}N_2O_3,HCl$ (m. p. 158°) are precipitated. The base itself, which may be obtained free from the second compound by heating orthonitrobenzylic chloride with orthanisidine in alcoholic soda solution, crystallises in lustrous, red prisms or tables with oblique ends; it melts at 80°. The second compound referred to above is *bisorthonitrobenzylorthanisidine*,

$$[NO_2\cdot C_6H_4\cdot CH_2]_2\colon N\cdot C_6H_4\cdot OMe,$$

and crystallises from the filtrate from the foregoing hydrochloride in small, thick, very yellow tablets which dissolve moderately well in hot alcohol and more freely in glacial acetic acid and benzene; it melts at 117° and has no basic properties.

Orthamidobenzylorthanisidine, $NH_2\cdot C_6H_4\cdot CH_2\cdot NH\cdot C_6H_4\cdot OMe$, is prepared by reducing the nitro-compound with zinc dust in glacial acetic acid at a temperature not exceeding 30°; the base is extracted by ether from the solution, and precipitated by dilution and addition of excess of alkali. It crystallises in large, white, flat needles and melts at 95°.

Formorthonitrobenzylorthanisidide,

$$NO_2\cdot C_6H_4\cdot CH_2\cdot N(C_6H_4\cdot OMe)\cdot CHO,$$

prepared by heating the nitro-compound with anhydrous formic acid, crystallises in large, well-formed, colourless, oblique prisms, and melts at 82°. By reduction with zinc dust in cold glacial acetic acid solution, it yields the corresponding *amido*-derivative and hydroquinazoline. The former crystallises from the ethereal extract of the solution rendered alkaline, in aggregates of white needles and melts at 98°; it dissolves in dilute mineral acids, and when these solutions are heated it is converted into the hydroquinazoline. *3′-Anisyldihydroquinazoline*, $C_6H_4<\begin{matrix} N = CH \\ | \\ CH_2\cdot N\cdot C_6H_4\cdot OMe \end{matrix}$, is best obtained by reducing formorthonitrobenzylorthanisidide with tin and hydrochloric acid in alcoholic solution; it is an oil, and is easily soluble in the usual organic solvents. The *hydrochloride*, $C_{15}H_{14}N_2O,HCl$, crystallises in white, fan-shaped laminæ or needles and melts at 128°; the *stannochloride*,

$$C_{15}H_{14}N_2O,HCl,SnCl_2$$

forms large, colourless tables and melts at 140°; the *picrate* melts at 197°. *3′-Anisyltetrahydroquinazoline*, $C_6H_4<\begin{matrix} NH\cdot CH_2 \\ | \\ CH_2\cdot N\cdot C_6H_4\cdot OMe \end{matrix}$, formed by reducing the dihydroquinazoline with sodium in alcoholic solution, crystallises in white, stellate needles, melts at 96° and is freely soluble in ether, alcohol, ethylic acetate, and benzene. A. G. B.

Synthesis of 3′-Paranisyldihydroquinazoline. By CARL PAAL and WILHELM SCHILLING (*J. pr. Chem.*, 1896, [2], **54**, 283—288).—*Orthonitrobenzylparanisidine*, from orthonitrobenzylic chloride and paranisidine (compare preceding abstract), crystallises in large, scarlet laminæ, melts at 73°, and is insoluble in water, sparingly soluble in light petroleum, but easily in most other organic solvents; the *hydrochloride*, $C_{14}H_{14}N_2O_3,HCl$, forms white needles, melting at 185°. When heated with formic acid, the base is converted into *formorthonitrobenzylparanisidide*, which crystallises in short, colourless, transparent prisms, melts at 69° and is freely soluble in warm carbon bisulphide, ether, alcohol, glacial acetic acid, ethylic acetate, and benzene; it has no basic properties. The best reducing agent to convert the formyl-derivative into the quinazoline is zinc dust and hydrochloric acid in an alcoholic solution; *3′-paranisyldihydroquinazoline* crystallises in thick, transparent tablets, melts at 115°, and dissolves easily in alcohol, ethylic acetate, and benzene; the *hydrochloride*, $C_{15}H_{14}N_2O,HCl$, crystallises in slender, white needles and in stellate prisms, and melts at 237°; the *zincochloride*, the *platinochloride*, and the *picrate* (m. p. 181°) are described.

Parahydroxyphenyldihydroquinazoline, $C_6H_4<\begin{matrix} N = CH \\ | \\ CH_2\cdot N\cdot C_6H_4\cdot OH \end{matrix}$, is formed by heating the anisyldihydroquinazoline with five times its weight of strong hydrobromic acid in a sealed tube for 1 hour at 130°

It crystallises in hard, yellowish prisms, melts at 235° and dissolves freely in dilute mineral acids and caustic alkalis, but only sparingly in most organic solvents.

3'-Paranisyltetrahydroquinazoline, obtained from the dihydro-base by the action of sodium in alcohol, crystallises in nacreous laminæ, melts at 134°, and dissolves freely in most hot organic solvents.

A. G. B.

Condensation of Benzaldehyde with Ethylic Acetoacetate in presence of Aromatic Amines. By BRONISLAW LACHOWICZ (*Monatsh.*, 1896, **17**, 343—360).—*Ethylic hydrobenzimidoacetoacetate*, $CHPh\colon N\cdot CHPh\cdot NH\cdot CMe\colon CH\cdot COOEt$

$$(\text{or } CHPh\colon N\cdot CHPh\cdot N\colon CMe\cdot CH_2\cdot COOEt)$$

is obtained when a mixture of 2 molecular proportions of ethylic acetoacetate and 1 of benzaldehyde is allowed to remain during about 12 hours at the ordinary temperature with excess of dilute alcoholic ammonia; it is deposited in long, colourless needles, and crystallises in thick prisms, melting at 129°; it is insoluble in water, but dissolves readily in alcohol and benzene, and is also dissolved by acids, but is reprecipitated on adding an alkali. It is not affected by boiling caustic potash, but, when heated with hydrochloric acid it breaks down with formation of benzaldehyde and ammonium chloride; it is also slowly decomposed by boiling alcohol. When heated with aniline or phenylhydrazine, it evolves ammonia, and benzylideneanilide or benzylidenehydrazone are produced. It reacts with warm ethylic acetoacetate, yielding Schiff and Puliti's ethylic phenylhydrolutidinedicarboxylate (Abstr., 1883, 1151); the production of this substance is probably preceded by the formation of an unstable, intermediate compound of the structure $CHPh(NH\cdot CMe\colon CH\cdot COOEt)_2$.

That the constitution of ethylic hydrobenzimidoacetoacetate is most probably represented by the first of the above formulæ, is shown by the behaviour of the substance towards nitrous acid, whereby a nitroso-compound is produced. It may be directly synthesised by allowing a solution of molecular proportions of ethylic acetoacetate and hydrobenzamide in alcohol to remain during 48 hours, when benzaldehyde and the above compound are produced in molecular proportion.

Benzylideneanilide and ethylic acetoacetate dissolved in alcohol react at ordinary temperatures, and, after a fortnight, the addition of water causes the precipitation of a new compound, probably *ethylic diphenyldihydrolutidinedicarboxylate*, $CHPh{<}{\substack{C(COOEt)\colon CMe\\ C(COOEt)\colon CMe}}{>}NPh$; this crystallises in colourless prisms, showing a weak, pale blue fluorescence, melts at 159—160°, and dissolves readily in alcohol, but only sparingly in ether or light petroleum. It is also produced when ethylic anilacetoacetate is warmed with a mixture of benzaldehyde and ethylic acetoacetate. It is slowly hydrolysed by alkalis, but when boiled with alcoholic potash during 12—14 hours, the liquid, on the addition of acetic acid, deposits 1:4-*diphenyldihydrolutidine*-3:5-*dicarboxylic acid*,

$$CHPh{<}{\substack{C(COOH)\colon CMe\\ C(COOH)\colon CMe}}{>}NPh,$$

which crystallises from alcohol in yellow, flat, microscopic prisms, and melts at 165°, evolving carbonic anhydride.

Ethylic 1:4-paratolylphenyldihydrolutidine-3:5-dicarboxylate,

$$CHPh{<}^{C(COOEt){:}CMe}_{C(COOEt){:}CMe}{>}N\ C_6H_4Me,$$

is obtained when paratoludine is substituted for aniline in the above action; it crystallises in colourless leaflets, melts without decomposing at 133°, and dissolves readily in alcohol, ether, benzene and light petroleum; it has much the same character as the former compound, but when treated with potash under the conditions requisite for the complete hydrolysis of that substance, yields the intermediate *mono-ethylic* salt, $C_{24}H_{25}O_4N$; the latter crystallises from alcohol in colourless leaflets, and melts and decomposes at 160°.

A mixture of ethylic acetoacetate and benzidine does not readily form a condensation product with phenylhydrazine in the cold, benzylidenehydrazone being invariably produced; if, however, the hydrazone of ethylic acetoacetate is first prepared and mixed with benzaldehyde, interaction takes place at the ordinary temperature with formation of a *substance* which separates, after 48 hours, in the form of highly-dispersive rhombohedral prisms. The same compound is produced from a mixture of benzaldehyde and 1:3:5-phenylmethylpyrazolone, and is doubtless *4-benzylidene-bis-1:3:5 phenylmethylpyrazolone*, $CHPh\left(CH{<}^{CO-NPh}_{CMe{:}N}\right)_2$. It crystallises from chloroform and melts to a red liquid at 154°, but after dissolution in ethylic alcohol yields crystals containing alcohol ($\frac{1}{2}$ mol.); these melt at 165°, and after liquefaction yield the same substance; the crystals from methylic alcohol also contain the solvent (1 mol.), and melt at 148°, evolving the alcohol. The pyrazolone dissolves readily in alcoholic hydrochloric acid, but in a short time a crystalline *substance*,

$$C_{27}H_{24}O_2N_4,HCl + EtOH,$$

is formed which is sparingly soluble in alcohol, and melts and decomposes at 232°. It also dissolves readily in aqueous ammonia, the solution in a short time depositing a *compound*, $C_{27}H_{24}O_2N_4,NH_3 + \frac{1}{2}H_2O$, which forms rose-coloured, highly-dispersive, quadratic prisms, and melts and decomposes at 166°; this substance is dissolved by alcohol, and the pyrazolone may be recovered from the resulting solutions. Analogous compounds are also obtained when other amines are employed; thus a mixture of piperidine and alcohol at once dissolves the pyrazolone, and the liquid subsequently deposits a *substance*,

$$C_{27}H_{24}O_2N_4,C_5H_{11}N + \tfrac{1}{2}EtOH,$$

in the form of long, colourless prisms, which melt and decompose at 196°. A dilute alkaline solution of 4-benzylidenebis-1 : 3 : 5-phenylmethylpyrazolone yields an amorphous precipitate when mixed with salts of the heavy metals, and its alcoholic solution gives a deep brownish-red coloration with ferric chloride. A. L.

Preparation of Thiazolines. By SIEGMUND GABRIEL and CARL VON HIRSCH (*Ber.*, 1896, **29**, 2609—2612).—Three methods already known are first recited. A better method than either of these, giving yields of 40—80 per cent. of the theoretical, is to heat a mixture of the hydrobromide of a bromalkylamine with a thiamide, rapidly to a suitable temperature (between 90° and 165°), and continue the heating until a portion of the mixture no longer gives any precipitate of a solid (thiamide) when water is added to it:

$$\begin{array}{l}CH_2Br\\ | \\ CH_2{\cdot}NH_2\end{array} + \begin{array}{l}HS\\ HN\end{array}\!\!>\!CR = \begin{array}{l}CH_2{\cdot}S\\ | \\ CH_2{\cdot}N\end{array}\!\!>\!CR + NH_4Br.$$

In this manner, the following substances were prepared :—μ-Phenylthiazoline, from bromethylamine and thiobenzamide. β-Methyl-μ-phenylthiazoline, from β-bromopropylamine and thiobenzamide. *μ-Methylthiazoline*, from bromethylamine and thiacetamide, is an oil boiling at 144°. *μ-Ethylthiazoline*, from bromethylamine and thiacetamide, boils at 162°; the yellow *picrate* melts at 135°. *$\beta\mu$-dimethylthiazoline*, from β-bromopropylamine and thiacetamide, boils at 152°, and is oxidised by bromine water to β-methyltaurine. *$\beta\mu$-diethylthiazoline*, from β-bromopropylamine and thiopropionamide, boils at 172°. C. F. B.

Quinoxaline Derivatives. By OSCAR HINSBERG (*Annalen*, 1896, **292**, 245—258.)—Quinoxaline *methiodide* crystallises in yellowish-red leaflets, and melts at 175°; the *ethiodide* separates from alcohol in red needles, and melts at 146°.

2′-Phenylquinoxaline, $C_6H_4<\begin{array}{l}N{:}CH\\ \;\;\;|\\ N{:}CPh\end{array}$, is obtained by heating an alcoholic solution of bromacetophenone with orthophenylenediamine in molecular proportion; it crystallises in slender needles, and melts at 78°.

The *ureide* of 3′-hydroxyquinoxaline-2′-carboxylic acid,

$$C_6H_4<\begin{array}{l}N{:}C{\cdot}OH\\ \;\;\;|\\ N{:}C{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH_2\end{array},$$

is obtained from alloxan and orthophenylenediamine; it crystallises in slender, yellow needles, and melts at 250°, becoming dark-coloured. By prolonged treatment with hot soda, it is converted into *3′-hydroxyquinoxaline-2′-carboxylic acid*, $C_6H_4<\begin{array}{l}N{:}C{\cdot}OH\\ \;\;\;|\\ N{:}C{\cdot}COOH\end{array}$, which crystallises from alcohol in small, yellow needles, and melts at 265°, liberating carbonic anhydride; the *3′-hydroxyquinoxaline* thus formed sublimes in colourless needles which melt at 265°.

3′:2′-Hydroxymethylquinoxaline, $C_6H_4<\begin{array}{l}N{:}C{\cdot}OH\\ \;\;\;|\\ N{:}CMe\end{array}$, is formed by the action of pyruvic acid on orthophenylenediamine; it melts at 245°.

Nitroparanisidine [$OMe:NO_2:NH_2 = 1:3:4$] is obtained by nitrating acetoparanisidide, and hydrolysing the product; it crystallises from alcohol in deep red needles, and melts at 129°. Pyruvic acid combines

with the product of reduction, forming *3'-hydroxy-2(or 3)-methoxy-2'-methylquinoxaline*, $OMe\cdot C_6H_3<\begin{matrix}N{:}C\cdot OH\\ |\\ N{:}CMe\end{matrix}$, which crystallises in small needles, and melts at 197°; the salts with mineral acids are yellow and the alkali derivatives colourless.

2-Dimethyl-3'-ketotetrahydroquinoxaline, $C_6H_4<\begin{matrix}NH\cdot CO\\ |\\ NH\cdot CMe_2\end{matrix}$, is obtained from ethylic bromisobutyrate and orthophenylenediamine, and crystallises from alcohol in colourless needles, melting at 177°; the substance, which does not exhibit acidic properties, forms colourless salts with mineral acids.

The *compound*, $C_{12}H_{14}N_2O_3$, which may have the constitution

$$C_6H_4<\begin{matrix}N(CH_2\cdot COOEt)\cdot CO\\ |\\ NH\text{———————}CH_2\end{matrix},$$

is derived from ethylic chloracetate and orthophenylenediamine, and crystallises in colourless prisms melting at 163°; alcoholic soda converts it into the *compound* $C_{10}H_{10}N_2O_3$, which crystallises from alcohol in needles, and melts at 212°. Sodium nitrite, in glacial acetic acid, converts the substance having the composition $C_{12}H_{14}N_2O_3$ into a compound which crystallises in colourless prisms, and melts at 155°, but does not exhibit the character of a nitroso-derivative; this compound and the original substance are oxidised by potassium dichromate and glacial acetic acid, giving rise to an acid which melts at 275°.

3-Nitroquinoxaline, $C_8N_2H_5\cdot NO_2$, is prepared by dissolving 4-nitro-orthophenylenediamine and the sodium hydrogen sulphite compound of glyoxal in water, in molecular proportion, and heating the mixture during several hours; it crystallises from dilute alcohol in long, brownish-yellow needles, and melts at 177°.

3:2':3-Nitrodiphenylquinoxaline is obtained from benzil and 4-nitro-orthophenylenediamine, and forms colourless leaflets melting at 188°. Reduction with tin and hydrochloric acid converts it into *3:2':3'-amidodiphenylquinoxaline*, $NH_2\cdot C_6H_3<\begin{matrix}N{:}CPh\\ |\\ N{:}CPh\end{matrix}$, which is also produced when a solution of triamidobenzene hydrochloride and benzil in dilute alcohol is heated in a reflux apparatus; it crystallises from alcohol and melts at 175°, both the alcoholic and ethereal solutions exhibiting greenish-yellow fluorescence. The *hydrochloride* crystallises in deep red leaflets, and melts at 250°, and the *acetyl* compound crystallises from chloroform in silky leaflets, and melts at 252°.

The *ureide* of 2(or 3)-amido-3' : 2'-hydroxyquinoxalinecarboxylic acid, $NH_2\cdot C_8N_2H_3(OH)\cdot CO\cdot NH\cdot CO\cdot NH_2$, is obtained by heating a solution of 1 : 3 : 4-triamidobenzene with alloxan, and does not melt below 300°; the solutions in ethylic alcohol and acetic acid exhibit feeble, greenish yellow fluorescence. The action of hot ammonia converts it into the *acid*.

2' : 3'-Hydroxyketo-1'-benzylquinoxaline, $C_6H_4<\begin{matrix}N(CH_2Ph)\cdot CO\\ |\\ N\text{=======}C\cdot OH\end{matrix}$, is produced on fusing a mixture of benzylorthopenylenediamine and

excess of oxalic acid at 160°; it crystallises from glacial acetic acid, and melts at 265°. Phosphorus pentachloride at 160° gives rise to benzylic chloride and 2′:3′-dichloroquinoxaline.

The author draws attention to certain regularities exhibited by the melting points of quinoxaline derivatives. M. O. F.

Derivatives of Thiobiazoline. By MARTIN FREUND and CARL MEINECKE (*Ber.*, 1896, **29**, 2511—2517. Compare Pulvermacher Abstr., 1894, i, 304; also Freund and Imgart, Abstr., 1895, i, 400).—*Formylthiosemicarbazide*, $NH_2\cdot CS\cdot NH\cdot NH\cdot CHO$, crystallises from hot water or methylic alcohol in irregular plates, and melts at 174—175°; it reduces cold Fehling's solution, and is devoid of basic properties. *Acetylthiosemicarbazide*, $NH_2\cdot CS\cdot NH\cdot NHAc$, crystallises from water in colourless needles, and melts at 165°; it reduces Fehling's solution.

5-*Imidothiobiazoline*, $NH\colon C<\begin{matrix}S-CH\\ \qquad\Vert\\ NH\cdot N\end{matrix}$, is obtained by the action of acetic chloride on formylthiosemicarbazide, and the *hydrochloride* crystallises from water in aggregates of needles melting at 149—150°; the base crystallises from water in needles, and melts at 191°. The *nitroso*-derivative melts and decomposes at 220°, the *methiodide* at 243°, and the *acetyl* derivative at 268°.

5-*Methylimidothiobiazoline*, $NH\colon C<\begin{matrix}S-CMe\\ \qquad\Vert\\ NH\cdot N\end{matrix}$, is obtained by heating thiosemicarbazide with acetic chloride on the water bath, and crystallises from water in lustrous, white leaflets, melting at 235°; the *hyrochloride* crystallises in white needles and melts at 110°, and the *nitroso*-derivative melts and decomposes at 227°. The *methiodide* melts at 215°, and the *methochloride* at 285°; the *acetyl* derivative crystallises from water in white needles, and melts at 292°, whilst the sodium derivative of the latter crystallises in long, slender needles, and melts at 179°. M. O. F.

Action of Diazomethane on Phenylthiocarbimide. By HANS VON PECHMANN and AUGUST NOLD (*Ber.*, 1896, **29**, 2588—2593).—When an ethereal solution of diazomethane (prepared from 5 c.c. nitrosomethylurethane) is allowed to remain with 3·2 grams of phenylthiocarbimide, crystals are formed which melt and decompose at 172·5° (losing two-thirds of their nitrogen), evolve hydrogen sulphide when treated with acid reducing-agents, and are neutral in character. The substance is probably *anilidothiobiazole*, with the constitution

$$NHPh\cdot C\begin{matrix}\diagup S-N\\ \qquad\Vert\\ \diagdown CH\cdot N\end{matrix};$$

it is certainly different from Pulvermacher's anilidothiobiazoline (Abstr., 1894, i, 304). From its alcoholic solution, mercuric chloride precipitates a compound, $C_8H_6N_3SHgCl$, melting at 193°; warm nitric acid converts it into an orange-yellow *trinitro*-derivative, which melts at 221°, and has acid properties; its white *nitroso*-derivative melts at 98°, its *acetyl* and *benzoyl* derivatives at 162° and 157° respectively; the

last compound yields benzanilide when reduced with zinc dust and sulphuric acid. C. F. B.

Hydrogenised Azines. By OSCAR HINSBERG and H. GARFUNKEL (*Annalen*, 1896, **292**, 258—271).—As Claus has shown, ammonium sulphide converts phenazine into dihydrophenazine; this substance reduces ammoniacal silver, and the *diacetyl* derivative crystallises from alcohol in prisms, and melts at 180°. The green double salt of dihydrophenazine hydrochloride, described by Claus, has been obtained by the authors on reducing phenazine with stannous chloride and sodium amalgam.

Naphthaphenazine *hydrochloride* crystallises from concentrated hydrochloric acid in small, brown prisms, and is decomposed by boiling water; it is indifferent towards alcoholic ammonium sulphide under ordinary conditions, but undergoes change when heated with this agent in sealed tubes at 160°. Reducing agents in acid solution convert it into a violet double salt, which is decomposed under the influence of boiling water.

Phenanthraphenazine *hydrochloride* crystallises from concentrated hydrochloric acid in small, brick-red needles, and is decomposed by hot water; acid reducing agents convert it into a violet double salt, which resembles the analogous compounds of dihydrophenazine and dihydronaphthaphenazine. The *acetyl* derivative of dihydrophenanthraphenazine crystallises in pale yellow leaflets, and melts at 252°; hot concentrated sulphuric and nitrous acids regenerate phenanthraphenazine.

Phenylphenanthraphenazonium hydroxide, $C_{14}H_8<\begin{smallmatrix}N\text{———}\\NPh(OH)\end{smallmatrix}>C_6H_4$, is obtained in the form of acetate when orthamidodiphenylamine hydrochloride and phenanthraquinone are heated in glacial acetic acid with sodium acetate, and the liquid diluted with water. The *hydriodide* is sparingly soluble in water, and the *hydrochloride* crystallises in yellowish-brown prisms; the *hydrobromide* separates from water in yellowish-brown crystals.

n-Phenyldihydrophenanthraphenazine, $C_{14}H_9<\begin{smallmatrix}N\text{—}\\NPh\end{smallmatrix}>C_6H_4$, is obtained by reducing the foregoing base with stannous chloride, and crystallises from chloroform in colourless leaflets, melting at 230°; the *hydrochloride* is colourless, and sparingly soluble in water, the solution in glacial acetic acid developing with ferric chloride a bluish violet coloration. M. O. F.

Preparation of Triazole and its Homologues. BY MARTIN FREUND (*Ber.*, 1896, **29**, 2483—2490. Compare Pulvermacher, Abstr., 1894, i, 304).—[With CARL MEINECKE.]—*Triazole-thiol* (*mercaptotriazole*), $CH<\begin{smallmatrix}N\text{—}N\\ \quad\ \ \Vert\\NH\cdot C\cdot SH\end{smallmatrix}$, is obtained by heating moderate quantities of formylthiosemicarbazide at 190°, the operation being interrupted when evolution of ammonia and sulphurous acid takes place; it is readily soluble in water and alcohol, insoluble in ether, benzene, and chloro-

form, and crystallises in slender needles, melting at 215—216°. The aqueous solution, which has an acid reaction, yields precipitates with many metallic salts dissolved in water; hot, concentrated sulphuric acid liberates sulphurous anhydride. The *bisulphide*, $C_4H_4N_6S_2$, is produced under the influence of a 3 per cent. solution of hydrogen peroxide; it crystallises from glacial acetic acid in prisms, and melts at 222°. On gently heating a solution of mercaptotriazole containing hydrogen peroxide, the bisulphide which is first formed is converted into triazole (compare Abstr., 1892, 735).

2-*Methyltriazole*-5-*thiol* (*mercapto-c-methyltriazole*, $\mathrm{CMe}<\begin{matrix}\mathrm{N{-}N} \\ \| \\ \mathrm{NH\cdot C\cdot SH}\end{matrix}$, is formed when acetylthiosemicarbazide is heated at 185°; it crystallises from water in white needles, and melts at 260—261°.

[With HEINRICH P. SCHWARZ.]—*Ethylthiosemicarbazide*,

$$\mathrm{NHEt\cdot CS\cdot NH\cdot NH_2},$$

is obtained from hydrazine hydrate and ethylthiocarbimide in alcoholic solution; it crystallises from alcohol, and melts at 84°. *Formylethylthiosemicarbazide*, $\mathrm{NHEt\cdot CS\cdot NH\cdot NH\cdot CHO}$, is derived from the foregoing derivative by the action of formic acid, and crystallises in lustrous leaflets, melting at 163—164°; it is feebly acidic in character.

5-*Ethylimidothiobiazoline*, $\mathrm{CH}<\begin{matrix}\mathrm{N\cdot NH} \\ \| \\ \mathrm{S\cdot C{:}NEt}\end{matrix}$, is obtained by the action of acetic chloride on finely-powdered formylethylthiosemicarbazide, the *hydrochloride*, which crystallises in rhombs and melts at 212°, being deposited by the solvent on evaporation; the base, which is hygroscopic, is sparingly soluble in ether, but dissolves readily in alcohol and water.

1-*Ethyltriazole*-5-*thiol* (*n-ethylmercaptotriazole*), $\mathrm{CH}<\begin{matrix}\mathrm{N{-}N} \\ \| \\ \mathrm{NEt\cdot C\cdot SH}\end{matrix}$, is produced when formylethylthiosemicarbazide is heated at 180—190° for 10—15 minutes; it crystallises from dilute alcohol in slender needles, and melts at 96—97°. The *sodium* derivative decomposes at 145°, and the *silver* derivative melts above 300°; copper and platinum salts also give rise to metallic derivatives.

1-*Ethyltriazole*, $\mathrm{CH}<\begin{matrix}\mathrm{N{-}N} \\ \| \\ \mathrm{NEt\cdot CH}\end{matrix}$, obtained from 1-ethylmercaptotriazole and 3 per cent. hydrogen peroxide, is a viscous, yellowish oil, which dissolves in water; the *hydrochloride*, which separates in rhombic crystals on adding ether to the alcoholic solution, melts at 196°.

1-*Methyltriazole*-5-*thiol* (*n-methylmercaptotriazole*), $\mathrm{CH}<\begin{matrix}\mathrm{N{-}N} \\ \| \\ \mathrm{NMe\cdot C\cdot SH}\end{matrix}$, is produced on heating formylmethylthiosemicarbazide (Pulvermacher, *loc. cit.*) above its melting point, and separates from water in crystals, which melt at 168°; it crystallises unchanged from hydrochloric acid, but the solution in soda deposits the *sodium* derivative, which sinters

at 130°, and decomposes at 200°. The *platinochloride* is crystalline, and the *silver* derivative amorphous.

1-*Methyltriazole*, $CH{<}\begin{array}{l}N\text{——}N\\ \quad\ \ \mid\\ NMe\cdot CH\end{array}$, is obtained from 1-methylmercaptotriazole and hydrogen peroxide, and readily absorbs water and carbonic anhydride; it melts at 90°, and the aqueous solution is alkaline. The *platinochloride* crystallises in prisms, and the *mercurichloride* crystallises from hot water in plates, and melts at 175°.

1-*Allyltriazole-5-thiol*, $CH{<}\begin{array}{l}N\text{————}N\\ \qquad\quad\ \ \Vert\\ N(C_3H_5)\cdot C\cdot SH\end{array}$, is obtained by heating formylallylthiosemicarbazide; it crystallises from water, and melts at 111°. M. O. F.

Derivatives of Triazosulphole [Thiotriazole.] By MARTIN FREUND and HEINRICH P. SCHWARZ (*Ber.*, 1896, **29**, 2491—2499).—*Allylamidothiotriazole*, $N{<}\begin{array}{l}N\cdot N\\ \quad\ \Vert\\ S\cdot C\cdot NH\cdot C_3H_5\end{array}$, is obtained by the action of nitrous acid on allylthiosemicarbazide, and crystallises in yellowish leaflets on adding petroleum to the alcoholic solution; it melts at 54°, and has basic properties. Hot water quickly liberates sulphur and nitrogen, with production of allylcyanamide. Dilute sulphuric acid also liberates sulphur and nitrogen; whilst hot, concentrated hydrochloric acid sets free one-half the available nitrogen, forming the *compound*, $CHMeCl\cdot CH_2\cdot NH\cdot C{<}\begin{array}{l}N\\ \mid\\ S\end{array}$; this substance is a syrup, and its *platinochloride* crystallises in anhydrous octahedra, and melts at 235°. Caustic soda causes a complete decomposition of allylamidothiotriazole, giving rise to sulphur, hydrogen sulphide and azoimide.

Methylamidothiotriazole, $N{<}\begin{array}{l}N\cdot N\\ \quad\ \Vert\\ S\cdot C\cdot NHMe\end{array}$, is produced by the action of nitrous acid on methylthiosemicarbazide, and melts at 96° when crystallised from ether; hot water converts it into trimethylisomelamine, obtained by von Hofmann from methylcyanamide. When the solution of methylamidothiotriazole in concentrated hydrochloric acid is gently heated, nitrogen is eliminated without liberation of sulphur; the concentrated liquid deposits methylthiocyanamide hydrochloride.

Ethylamidothiotriazole, $N{<}\begin{array}{l}N\cdot N\\ \quad\ \Vert\\ S\cdot C\cdot NHEt\end{array}$, crystallises from ether and melts at 66—67°; boiling water converts it into triethylisomelamine. M. O. F.

Amidotriazosulphole [Amidothiotriazole.] By MARTIN FREUND and ALFRED SCHANDER (*Ber.*, 1896, **29**, 2500—2505).—It having been shown that nitrous acid converts phenylthiosemicarbazide into a tetrazole derivative (Abstr., 1895, i, 193), it became of interest to ascertain whether thiosemicarbazide undergoes a similar change. Thiosemicarb-

azide can be obtained from hydrazine sulphate by an improved method, in quantity amounting to 70 per cent. of the theoretical; the *hydrochloride* crystallises from hydrochloric acid in slender needles, and melts at 186 to 190°, according to the rate at which the temperature is raised.

Amidothiotriazole, $N{<}\begin{matrix}N\cdot N \\ \| \\ S\cdot C\cdot NH_2\end{matrix}$, is obtained by cautiously adding sodium nitrite to an aqueous solution of thiosemicarbazide hydrochloride; it crystallises from ether in long, transparent needles, and melts at 128—130° with slight explosion. It dissolves in alcohol, glacial acetic acid, ethylic acetate, ethylic acetoacetate and aniline, without undergoing decomposition, and is sparingly soluble in chloroform and carbon bisulphide; it is insoluble in benzene, toluene, and xylene. Aqueous silver nitrate causes decomposition and liberation of gas; ammoniacal silver nitrate produces a white precipitate which rapidly decomposes, even when protected from light. Boiling water liberates nitrogen and sulphur, with production of cyanamide, whilst aniline, under the same conditions, converts amidothiotriazole into dicyandiamide; concentrated hydrochloric acid first forms the *hydrochloride* which decomposes at 96°, and when heated gives rise to the hydrochloride of thiocyanamide. Bromine converts it into the hydrobromide of thiocyanamide, and alkalis liberate sulphur and azoimide.

M. O. F.

Thiourazole. By MARTIN FREUND and ALFRED SCHANDER. (*Ber.*, 1896, **29**, 2506—2511). *Hydrazothiodicarbonamide*,

$$NH_2\cdot CS\cdot NH\cdot NH\cdot CO\cdot NH_2,$$

is obtained from thiosemicarbazide hydrochloride and potassium, cyanate; it sinters at 210°, and melts and decomposes at 218—220°.

Thiourazole, $CS{<}\begin{matrix}NH\cdot NH \\ | \\ NH\cdot CO\end{matrix}$, is obtained by heating a solution of the foregoing substance in concentrated hydrochloric acid for half an hour in a reflux apparatus, and filtering off the thiosemicarbazide hydrochloride which separates on cooling; it crystallises from hot water, and melts at 177°. The substance is both basic and acidic, and is indifferent towards ferric chloride and hydrogen peroxide.

When hydrazothiodicarbonamide is oxidised with ferric chloride, it yields a *hydrochloride*, $C_4H_8N_8SO_2,HCl$, which crystallises from water, and melts at 219—224°; the *base* crystallises from hot water, and melts at 204—205°. Fusion converts hydrazothiodicarbonamide into a white, crystalline compound, which sinters at 220°, and melts at 235—240°.

Phenylhydrazothiodicarbonamide, $NH_2\cdot CS\cdot NH\cdot NH\cdot CO\cdot NHPh$, is obtained from thiosemicarbazide and phenylic cyanate; it sinters at 210°, and melts at 217—218°. Concentrated hydrochloric acid converts it into diphenylcarbamide, semicarbazide hydrochloride, and thiourazole.

M. O. F.

Action of Hydrazines on Nitriles under the Influence of Sodium. By R. ENGELHARDT. (*J. pr. Chem.*, 1896, [2], **54**, 143—

176).—To prepare the compound obtained by Walther (*Abstr.*, 1894, i, 503) from the action of phenylhydrazine (1 mol.) on benzonitrile (2 mols.) in the presence of sodium, the hydrazine and nitrile are dissolved in benzene, and sodium is added until it no longer dissolves; the mixture is then heated in a reflux apparatus to complete the reaction, much ammonia being evolved during the process. A little alcohol is now added to dissolve the remaining sodium, the benzene is distilled off, and the residue crystallised from hot alcohol. A very small proportion of sodium is necessary, so that the formation of a definite sodium derivative does not seem to be essential for the change; nor is sodium cyanide formed to any extent. The yield is 90 per cent. of the mixed hydrazine and nitrile.

Analyses of the compound agree with the formula $C_{20}H_{15}N_3$ (compare *loc. cit.*), which is confirmed by cryoscopic determinations of the molecular weight. The stability of the compound indicates a closed ring structure, and, after discussing various possibilities, the author concludes that the reaction consists in the formation of a hydrazidine from the phenylhydrazine and benzonitrile, which then forms, with another molecule of benzonitrile, a phenyldibenzenylhydrazidine (compare Pinner, Abstr., 1894, i, 385); by loss of ammonia this would yield the new compound, which may, therefore, be regarded as a triphenyltriazole (*loc. cit.*).

1:3:5-*Triphenyltriazole*, $NPh<\begin{matrix} N = CPh \\ \quad\; | \\ CPh : N \end{matrix}$, crystallises in colourless prisms, melts at 104°, boils above 360°, and is soluble in most solvents, except water. Ordinary oxidising and reducing agents are without action on the compound. The *hydrochloride*, $C_{20}H_{15}N_3,HCl$, melts and decomposes at 169°; it is insoluble in cold water and is decomposed by warm water into the base and hydrogen chloride. The nitroderivatives are under examination. The *ethiodide*, $C_{20}H_{15}N_3,EtI$, melts at 145°; by dissolving it in dilute sulphuric acid and adding sodium hydroxide, a precipitate is obtained which, when dissolved in hydrochloric acid and treated with platinic chloride, yields the *platinochloride* of the *ethochloride* $(C_{20}H_{15}N_3)_2,Et_2PtCl_6$. The *methohydroxide* crystallises in white granules (with benzene of crystallisation), melts at 181°, and is soluble in alcohol but not in ether or water. The *platinochloride* of the *methochloride* was also prepared.

1:3:5-*Phenyldiorthotolyltriazole* is prepared by substituting orthotolunitrile for benzonitrile in the above prescription; it crystallises in white, felted needles, melts at 86°, and is very soluble in the usual solvents, except water. 1:3:5-*Phenyldiparatolyltriazole* is similarly prepared; it crystallises in nacreous laminæ, melts at 115°, and dissolves in the usual solvents, except water; the *hydrochloride* melts at 180°.

3:5:1-*Di-α-naphthylphenyltriazole* was prepared from phenylhydrazine and α-naphthonitrile, but could not be crystallised or otherwise purified. 3:5:1-*Di-β-naphthylphenyltriazole* crystallises in flocculent aggregates of white needles, melts at 160°, and dissolves easily in hot pyridine, amylic alcohol, chloroform, glacial acetic acid, benzene, acetone and ethylic acetate; more sparingly in ethylic and methylic alcohols, ether and light petroleum, but not in water.

Attempts to produce Pinner's diphenyltriazole (*loc. cit.*) by the action of hydrazine sulphate on benzonitrile in presence of sodium proved abortive.

1 : 3 : 5-β-*Naphthyldiphenyltriazole*, $C_{10}H_7 \cdot N<\begin{matrix} N = CPh \\ | \\ CPh : N \end{matrix}$, was prepared from β-naphthylhydrazine and benzonitrile by this method; it crystallises in white needles, melts at 144° and dissolves freely in benzene, ether, glacial acetic acid and hot alcohol, more sparingly in light petroleum, and not at all in water. No triazoles could be formed from acetonitrile or propionitrile and phenylhydrazine under the influence of sodium.

When a secondary, unsymmetrical hydrazine is caused to react with a nitrile in the manner under consideration, the two compounds condense in molecular proportion to form a hydrazidine. *Phenylbenzenylmethylhydrazidine*, $NMePh \cdot NH \cdot CPh : NH$, is prepared from benzonitrile (1 mol.) and β-methylphenylhydrazine (1 mol.) by dissolving the compounds in benzene and treating the solution with sodium; the operations are similar to those described at the beginning of this abstract. The hydrazidine is crystallised by dissolving it in benzene and adding light petroleum until the solution becomes turbid; after a time, long, yellow crystals separate, which become pale yellow needles on repeating the process; they melt at 105°, and exhibit basic properties. *Phenylbenzenylethylhydrazidine* resembles the methyl-derivative in every respect, and also melts at 105°, its *platinochloride* melts at 196°.

Diphenylbenzenylhydrazidine, $NPh_2 \cdot NH \cdot CPh : NH$, from β-diphenylhydrazine and benzonitrile, crystallises in slender, pale yellow needles, melts at 170°, and is only sparingly soluble in cold alcohol, ether and benzene, but is insoluble in light petroleum and water; the *hydrochloride*, $C_{19}H_{17}N_3,HCl$, is described. The *acetyl*-derivative,

$$NPh_2 \cdot N \cdot N : CPh \cdot NHAc,$$

crystallises in intensely yellow needles, and melts at 185°; this is the sole acetyl-derivative which could be obtained. The *nitroso*-derivative, $NPh_2 \cdot N(NO) \cdot CPh : NH$, crystallises in yellow needles, and melts at 206°.

No reaction occurs between nitriles and symmetrical hydrazines under the influence of sodium. A. G. B.

Creatinines of Different Origin. By M. TOPPELIUS and HERBERT POMMEREHNE (*Arch. Pharm.*, 1896, **234**, 380—397).—Johnson (Abstr., 1889, 165) has described several creatinines, but the authors find, them to be identical. They prepared a creatinine from urine; they converted this by prolonged boiling with water into creatine, and the creatine back into creatinine by evaporation with hydrochloric acid; they prepared creatinine from the creatine of meat extract; and, lastly, from creatine obtained synthetically from cyanamide and methylamidoacetic acid. The hydrochlorides of all these creatinines crystallised anhydrous from fairly strong hydrochloric acid, but with H_2O from water; in 2 per cent. solution at 15°, all gave an angle of

of refraction of 64° 45′ in the Pulfrich refractometer, and all were inactive to polarised light. The base itself in all cases dissolved in about 10·7 parts of water at 15° and about 625 parts of absolute alcohol at 17°, and had the same reducing action on Fehling's solution. The aurochlorides in all cases melted at about 162° and reacted in the same way with ether. The platinochloride in all cases melted at about 210°, and dissolved in about 36 parts of water at 13°. The picrate in all cases melted at about 213°. C. F. B.

Action of Methylic Iodide on Xanthine Salts (Pseudotheobromine). By HERBERT POMMEREHNE (*Arch. Pharm.*, 1896, **234**, 367—380).—There are three possible dimethylxanthines, $C_7H_8N_4O_2$. Of these, one is the naturally occurring theobromine, prepared also artificially by E. Fischer by acting on the lead derivative of xanthine with methylic iodide. The second, theophylline, occurs in tea-leaves, and has been prepared by E. Fischer from dimethyluric acid. What is probably the third isomeride is obtained, together with small quantities of, apparently, theobromine and theophylline, when the silver derivative of xanthine is heated with methylic iodide at 130—140°. The theobromine separates as the alcoholic extract is concentrated; the theophylline is precipitated with mercuric nitrate, and finally the new substance is precipitated by means of silver nitrate; to it the name of *pseudotheobromine* is given. It is a white substance which crystallises imperfectly and does not melt below 280°; when its solution is mixed with chlorine water, evaporated, and the residue treated with ammonia, a red coloration is produced. Its *hydrobromide, hydrochloride, platinochloride*, and *aurochloride* strictly resemble those of theobromine, except that the two first retain their halogen acid at 100°, instead of losing it, as the analogous salts of theobromine do. A small quantity of pseudotheobromine was obtained on one occasion when methylic iodide was boiled with a solution of xanthine in alcoholic potash; theobromine itself is, however, the main product, and on another occasion was the only one. C. F. B.

Action of Wagner's Reagent on Caffeine and a New Method for the Estimation of Caffeine. By MOSES GOMBERG (*J. Amer. Chem. Soc.*, 1896, **18**, 331—342).—The author draws attention to the fact that, although an aqueous solution of caffeine gives no precipitate with Wagner's reagent (a solution of iodine in potassium iodide), yet an acidified solution readily gives a precipitate of caffeine periodide, $C_8H_{10}N_4O_2,HI,I_4$. This periodide is not identical with the one obtained by Tilden (this Journal, 1865, **18**, 99). When dry it forms a violet-blue amorphous powder, melting at 213°; when moist, it rapidly loses iodine on exposure to the air, but it is permanent when dry and suffers only slight loss when heated at 100°. It also loses but little iodine when suspended in water; it readily dissolves in alcohol, especially on heating, and a considerable portion is decomposed into the free base and iodine. Its methyl alcoholic solution, on spontaneous evaporation, leaves the periodide in the form of beautiful six-sided prisms, with a metallic dark-bluish lustre. It is insoluble in carbon bisulphide, but dissolves in hot ethylic acetate without undergoing decomposition.

The author has used Wagner's reagent for the estimation of caffeine, but the method is only applicable when other substances, which might be precipitated by the iodine, are absent. Definite volumes of acidified (best with hydrochloric acid) solutions of caffeine are precipitated with a known volume of iodine in potassium iodide; after complete precipitation, an aliquot part of the supernatant liquid is obtained, either by filtration or decantation, and the excess of iodine in it titrated by decinormal sodium thiosulphate. In the calculation, 1 part of iodine = 0·3834 parts of caffeine, or 1 c.c. of N/10 iodine = 0·00485 gram of caffeine. The results obtained by this method are very exact, the best being obtained when the iodine is in large excess. The author also recommends the method for the estimation of caffeine in drugs containing it. J. J. S.

Caffeine Perhaloids. By MOSES GOMBERG (*J. Amer. Chem. Soc.*, 1896, **18**, 347—377).—Caffeine hydriodide di-iodide, $C_8H_{10}N_4O_2,HI,I_2$, is obtained when a solution of caffeine in dilute alcohol, containing some hydriodic acid, is exposed to sunlight in a warm place. The diiodide is only formed when the deposition of crystals is rapid, if the liberation of iodine is slow, the tetriodide is formed. It melts at 171°. The crystals, according to the author, are anhydrous, whereas Tilden (this Journal, 1865, **18**, 99) gives the composition as $(C_8H_{10}N_4O_2,HI,I_2)_2 + 3H_2O$.

Caffeine hydriodide tetriodide, $C_8H_{10}N_4O_2,HI,I_4$, is obtained by treating an acidified solution of caffeine with Wagner's reagent (compare preceding abstract). It is the most stable periodide of caffeine, and is the one usually obtained. It may also be obtained by passing hydrogen iodide into a chloroform solution of caffeine and iodine, or by triturating caffeine hydrobromide dibromide or tetrabromide with an aqueous solution of potassium iodide.

Caffeine hydrobromide tetriodide, $C_8H_{10}N_4O_2,HBr,I_4$, is readily obtained when a slow stream of hydrogen bromide is passed into a chloroform solution of caffeine and iodine. It is never formed in the presence of hydrogen iodide. It is usually amorphous, but can be crystallised, has a dark brown chocolate colour, and melts at 183°.

Caffeine hydrochloride di-iodide, $C_8H_{10}N_4O_2,HCl,I_2$, is obtained by passing hydrogen chloride into a chloroform solution of caffeine and iodine. It forms small, crystalline granules of a pale brown colour, and melts at 165°.

Caffeine hydrobromide tetrabromide, $C_8H_{10}N_4O_2,HBr,Br_4$. Whenever bromine is allowed to act on caffeine, this perbromide is one of the first products formed. It is produced in presence or in absence of hydrogen bromide, in presence of water, of chloroform, or when pure bromine is employed. It crystallises in small, orange-red, prismatic crystals, and melts sharply at 170°, but is previously converted into the dibromide. On exposure to the air, it loses 2 atoms of bromine, yielding the corresponding *dibromide*, which is more stable. The author controverts the statements of Maly and Hinteregger (Abstr., 1882, 629), and also of E. Fischer (*Annalen*, **215**, 264), that on the addition of pure bromine to caffeine a dibromide, $C_8H_{10}N_4O_2,Br_2$, is formed. The only products are the tetrabromide already mentioned and the corresponding derivative of monobromocaffeine.

Caffeine hydrobromide dibromide, $C_8H_{10}N_4O_2,HBr,Br_2$, obtained by exposing the tetrabromide to the air or by treating it with ether, is an amorphous, yellow powder, and melts at 170°.

Caffeine hydrochloride tetrabromide is somewhat difficult to prepare. The bromine must be perfectly free from hydrogen bromide, and must be used in dilute solution only, moreover the chloroform must be free from alcohol and moisture. It has a lighter colour than the corresponding hydrobromide, and melts at 149°.

Chlorocaffeine hydriodide, $C_8H_9ClN_4O_2,HI$, can only be obtained in the absence of water. It forms white, heavy crystals, and is readily decomposed by water and by alcohol. The corresponding *hydrobromide* is even less stable, and the *hydrochloride* the least stable.

Chlorocaffeine hydriodide pentiodide, $C_8H_9ClN_4O_2,HI,I_5$, is a black, amorphous powder with a slightly bluish tint, and melts at 185—186°. The corresponding *hydrobromide*, $C_8H_9ClN_4O_2,HBr,I_5$, is not so black as the hydriodide, melts at 169°, and is very unstable.

Chlorocaffeine hydrochloride tetriodide, $C_8H_9ClN_4O_2,HCl,I_4$, is bluish-black, and melts at 137°.

Chlorocaffeine hydrobromide pentabromide, $C_8H_9ClN_4O_2,HBr,Br_5$, obtained by treating a chloroform solution of chlorocaffeine with bromine, crystallises in dark red, short, thick prisms, and melts at 151°. On digesting with ether for several days, it is converted into *chlorocaffeine hydrobromide monobromide*, $C_8H_9ClN_4O_2,HBr,Br$, which is a yellow, amorphous powder, and melts at 189°.

Chlorocaffeine hydrochloride pentabromide, $C_8H_9ClN_4O_2,HCl,Br_5$, forms small, scarlet-red prisms, and melts at 153°.

Bromocaffeine hydriodide, *hydrobromide*, and *hydrochloride* have been prepared, and are all fairly stable.

Bromocaffeine hydriodide pentiodide forms a dull black, amorphous powder, and melts at 183°.

Bromocaffeine hydrobromide pentiodide is a dark brown, amorphous powder, which melts at 160°.

Bromocaffeine hydrochloride tetriodide is very unstable; it consists of brown or dark blue crystals, and melts at 136°.

Bromocaffeine hydrobromide pentabromide, obtained in a similar manner to the corresponding derivative of chlorocaffeine, forms dark orange-red prisms, and melts at 156°.

Bromocaffeine hydrobromide monobromide, obtained from the pentabromide by treatment with anhydrous ether, is a light yellow powder, which melts and decomposes at 206°.

Bromocaffeine hydrochloride pentabromide is readily decomposed, and melts at 157°.

These compounds are, as a rule, decomposed by water and other solvents, by exposure to moist air, or by heating at 100°. Details are given in the original. J. J. S.

Action of Methylic Iodide on Papaveric Acid. By GUIDO GOLDSCHMIEDT and ALFRED KIRPAL (*Monatsh.*, 1896, **17**, 491—505).—The substance melting at 122—124°, obtained by Schranzhofer (Abstr., 1894, i, 59), may be prepared by heating the monomethylic salt of papaveric acid (compare Abstr., 1893, i, 180), with methylic alcohol

and a little sulphuric acid, and is therefore the dimethylic salt of papaveric acid, $C_6H_3(OMe)_2\cdot CO\cdot C_5NH_2(COOMe)_2$; when heated with hydrochloric acid, it yields papaveric acid, and not the methylbetaïne as was supposed by Schranzhofer; the same result is obtained if alkali be employed.

Schranzhofer's second substance (m. p. = 195—197°, *loc. cit.*) is found on examination to contain three methoxyl-groups and is readily prepared by the etherification of papaveric acid; it is therefore a monomethylic salt of that acid, $C_6H_3(OMe)_2\cdot CO\cdot C_5NH_2(COOMe)\cdot COOH$, and is doubtless the γ-alkyl salt, that prepared by the etherification of papaveric anhydride being therefore the β-derivative. Attempts to prepare *methylic pyropapaverate* from the foregoing γ-methylic papaverate were unsuccessful; it may, however, be made by heating pyropapaveric acid with methylic alcohol and sulphuric acid; it crystallises from methylic alcohol in beautiful, long, white, silky needles, and melts at 108°.

Analyses of the substance melting at 192—194° (Schranzhofer, *loc. cit.*), made with a view of determining the number of methyl groups attached to oxygen and nitrogen respectively, show that its molecule is more complicated than was supposed by its discoverer, and may be written $C_{28}H_{12}N_2MeO_9(OMe)_5$. Constitutional formulæ for the substance are suggested, and the paper concludes with analyses of the platinochloride $(C_{34}H_{30}N_2O_{14})_2,H_2PtCl_6 + 8H_2O$, which confirm the above formula. A. L.

Optical Rotation of Atropine and its Salts. By J. GADAMER (*Arch. Pharm.*, 1896, **234**, 543—551).—The author has succeeded in preparing pure atropine by treating *Atropin. purissimum Merck* with moderately concentrated alcoholic soda for several months. After recrystallisation and repeated conversion into the sulphate and reconversion into the free base, perfectly pure atropine is obtained. In this form, it is optically inactive, and its salts are also quite devoid of optical activity. Atropine prepared in this way melts at 115·5—116°, the anhydrous sulphate melts at 180—181°, and the hydrated salt ($1H_2O$) at 161°, or 151—154°, according to the rate at which it is heated. The oxalate melts at 188—188·5° and is anhydrous; Hesse gives the melting point as 176°. Hyoscyamine oxalate melts at 173° (176° Hesse) The author has obtained the *aurochloride* of a new alkaloid from crude duboisine, but this has not yet been completely analysed; it melts at 198° and forms characteristic spherical aggregates. A. H.

Scopolamine and i-Scopolamine. By OSWALD HESSE (*Ber.*, 1896, **29**, 2439—2442. Compare Abstr., 1896, i, 655).—The author maintains, in opposition to E. Schmidt (Abstr., 1896, i, 712), that the so-called ordinary scopolamine hydrobromide is simply a mixture of the hydrobromides of hyoscine and atroscine. A. H.

Organic Chemistry.

Theory of the Pyrogenic Reactions of Aliphatic Hydrocarbons. By FRITZ HABER (*Ber.*, 1896, **29**, 2691—2700).—Berthelot's theory, with its assumption of a limiting equilibrium, and Lewes' theory of the luminosity of flame, are criticised, and, in part, rejected. These investigators obtained abnormal results because they experimented with paraffins containing only one or two atoms of carbon in the molecule. The author has experimented with hexane, and also with trimethylethylene, acetylene, and benzene. To avoid secondary reactions, the gas was exposed for a few seconds only to the high temperature; this was attained by passing it in a current through a heated tube. At a temperature of 600—800°, neither carbon nor an appreciable quantity of hydrogen was liberated; what happens is a shifting of a hydrogen atom, with formation of an olefine and either methane or ethane, the latter, if formed at all, being always formed in smaller amount. Thus hexane yields amylene and methane. Trimethylethylene also yields methane, but it yields ethylene in addition, although this requires a complete change in the arrangement of the atoms of carbon. Long ago, too, Thorpe and Young (*Annalen*, 1873, **165**, 1) noticed that the distillation of paraffin yields no hydrogen, but lower hydrocarbons; in this case, however, of approximately equal molecular weight. In the case of the paraffins, then, the union between carbon and carbon is more easily dissolved than that between carbon and hydrogen. The opposite is the case with aromatic hydrocarbons; benzene, for instance, yields diphenyl and hydrogen. It decomposes, however, much less easily than hexane. In addition to the products mentioned above, hexane yields a little benzene; this, however, is obtained equally from trimethylethylene, and is doubtless formed by a secondary reaction from the acetylene first produced.

At 900—1000°, the reaction is quite different; coke, tar, and hydrogen are formed, and methane is the only paraffin to be found, ethylene the only olefine; ethylene and hydrogen therefore do not unite to form ethane at this temperature. Acetylene (at 800°) yields but a little ethylene with much hydrogen; a great part of the gas is unchanged. Methane alone is entirely stable.

Incidentally, it is shown how the results of a gas analysis, including an explosion of the residual gas after absorption, may be utilised to infer the presence or absence in the gas of ring compounds with the composition $C_n H_{2n}$, such as trimethylene. The results of such analyses lead one to assume the presence of such hydrocarbons in coal-gas.

C. F. B.

Limiting the Explosive Proportions of Acetylene, and Detecting and Measuring the Gas in Air. By FRANK CLOWES. (*Chem. News*, 1896, **74**, 188. See this vol. ii, 128.)

Decomposition of Sugars under the Influence of Acids. By MARCELLIN BERTHELOT and GUSTAVE ANDRÉ (*Compt. rend.*, 1896, **123**,

567—580).—The authors have investigated more especially the formation of carbonic anhydride, humic, levulinic, and formic acids by the action of dilute mineral acids on various sugars. Phosphoric acid was preferred to hydrochloric or sulphuric acid, because it does not volatilise with steam and exerts no oxidising action on the sugars. Some of the experiments were made at 100°, in sealed tubes from which the air had been removed; others in flasks at the ordinary pressure, sometimes with a reflux condenser, sometimes with an ordinary condenser so that the volatile products were removed as fast as they were formed. The substances estimated, as a rule, were glucose, carbonic anhydride, carbonic oxide, formic acid, humic acid, which was dried and weighed at 100°, levulinic acid, which was estimated by the method of coefficients of distribution between water and ether (*Ann. Chim. Phys.*, 1872, [4], **26**, 396 and 433), furfuraldehyde, and water.

Glucose, when heated in sealed tubes at 100° with about five times its weight of phosphoric acid and six times its weight of water, yields carbonic anhydride and carbonic oxide in small quantity, and formic, levulinic, and humic acids. Even after 115 hours, 12 per cent. of the glucose remains unchanged, and the phenomena indicate that a large part, at least, of the glucose is first changed into glucosan, which then undergoes decomposition. The quantity of formic acid is higher than corresponds with the quantity of levulinic acid, but part of it is formed at the same time as the humic acid. Direct experiments show that there is a considerable and variable difference between the rates of formation of the levulinic and humic acids. The carbonic oxide results mainly from secondary decomposition of the formic acid, but part of it is formed by the action of the acid on the glucose. Direct experiments show that the levulinic acid yields neither carbonic oxide nor humic acid. The greater part of the carbonic anhydride is produced in the earlier stages of the decomposition, and results chiefly from the direct action of the acid on the glucose, although a small quantity is formed by the prolonged action of acids on levulinic acid.

In flasks at the ordinary pressure, there is an increase in the proportion of carbonic anhydride, and this is not due to oxidation, since the same result is obtained in an atmosphere of hydrogen; furfuraldehyde is also formed. As in the experiments with tubes, there is no fixed relation between the formic acid and humic acid; there also seems to be evidence of the formation of a small quantity of acetic acid. The proportion of volatile acids formed seems to be greatest when sulphuric acid is used, but the proportion of humic acid shows no similar variation. The higher proportion of carbonic anhydride formed during distillation cannot be attributed to decomposition of levulinic acid.

The isomerides of glucose, galactose, levulose, and maltose behave in a similar way, and when distilled with acids yield a notable proportion of carbonic anhydride, and also a small quantity of furfuraldehyde. As Tollens and Grote have observed, the production of humic acid from levulose is more rapid than in the case of the other sugars, but all the other changes are also more rapid with levulose than with the others.

The more concentrated the acids, the greater is the proportion of

humic acid formed. The complicated nature of the reaction is a natural result of the complicated constitution of the glucoses; the production of formic acid, for example, may be attributed to the splitting off of the last aldehydic molecule of the generatrix of the glucose. C. H. B.

Arabinose. By MARCELLIN BERTHELOT and GUSTAVE ANDRÉ (*Compt. rend.*, 1896, **123**, 625—631).—The authors have studied the action of water and acids on arabinose and on furfuraldehyde under various experimental conditions. No furfuraldehyde was formed when dilute aqueous solution of arabinose was distilled at 100°, but when heated with water for 5 hours at 200°, almost one-half of the theoretical yield of furfuraldehyde was obtained. Three experiments are described in which arabinose was heated in sealed tubes with (1) saturated aqueous hydrochloric acid, (2) 25 times its weight of 12·3 per cent. hydrochloric acid, and (3) dilute aqueous phosphoric acid. Of the products formed, namely, carbonic anhydride, carbonic oxide, formic acid, furfuraldehyde, organic acids, and humic matters, about 92 per cent. of the carbon of the arabinose taken appeared as humic matter, and in no case was more than a trace of furfuraldehyde obtained, the latter being decomposed and polymerised under the conditions of experiment. Gum arabic, when heated in a sealed tube at 100° with concentrated aqueous hydrochloric acid, gave similar results, but with more dilute hydrochloric acid a larger proportion of carbonic anhydride was formed. When arabinose (5 grams) was slowly distilled with dilute aqueous phosphoric acid, for 590 hours, the evaporated water being replaced from time to time, it yielded 0·2999 gram of carbonic anhydride, and 1·9632 gram of furfuraldehyde. It is remarked in conclusion that when arabinose is submitted to the action of dilute acids, three classes of reactions occur simultaneously. (1) The formation of furfuraldehyde, which marks a distinction between the pentoses and hexoses. (2) The formation of humic acid, more especially in sealed tubes. (3) The formation of carbonic anhydride, more marked under conditions of slow distillation, a decomposition common to the pentoses and the hexoses. A. C. C.

Isoallylamine (1-Aminopropylene). By SIEGMUND GABRIEL and CARL VON HIRSCH (*Ber.*, 1896, **29**, 2747—2751).—The authors have succeeded in preparing this base, which had previously only been obtained in aqueous solution, by distilling β-propylamine hydrobromide with 33 per cent. aqueous potash, and fractionating the distillate. Isoallylamine, $CHMe\!:\!CH\cdot NH_2$ is a colourless, mobile liquid, which fumes in the air, has the characteristic odour of the amines, is very hygroscopic, and is miscible with water; it boils at 66—67° (751 mm. pressure), has a sp. gr. 0·812 at 16°, and burns with a luminous flame. The base readily undergoes change when its solution in water is heated. In addition to the salt with bismuth iodide, which has been previously described, it was only possible to obtain the *platinochloride*, which is an orange red, crystalline powder. It acts as a poison, and exerts a remarkable specific action on the so-called papillary part of the kidneys, in this respect resembling vinylamine. It reacts in the normal manner with chloroform and potash, and with nitrous acid, but does not undergo the

thiocarbimide reaction. With carbon bisulphide, it forms $\beta\beta$-methyl-μ-mercaptothiazoline (Hirsch, Abstr., 1890, 859); this substance melts at 95—97°, and not at 82° as stated by Hirsch. The base readily unites with the halogen acids, forming the corresponding substituted propylamine. *β-Chloropropylamine picrate* melts at 158°. *β-Iodopropylamine hydriodide* is a crystalline powder. The *picrate* melts at 150°. Sulphurous acid converts the base into β-methyltaurine, $C_3H_9NO_3S$.

The base is accompanied by a *polymeride*, $(C_3H_7N)_2$, which boils at 143—145°, and has the normal vapour density corresponding with the above formula. A. H.

Action of Sodium on Acetaldehyde. By PAUL C. FREER (*Annalen*, 1896, **293**, 326—338. Compare Abstr., 1894, i, 65).—The production of sodium acetone, $CH_2{:}CMe\cdot ONa$, by the action of metallic sodium on a dilute xylene solution of acetone (*loc. cit.*), suggested the possibility of obtaining the sodium derivative of vinylic alcohol, $CH_2{:}CH\cdot ONa$, by treating acetaldehyde with the metal. Acetaldehyde is vigorously attacked by sodium, hydrogen being liberated and a crystalline substance formed, but, owing to the unstable character of this product, it is necessary to study the action in presence of benzoic chloride, which gives rise to a solid benzoyl derivative of an aldehydo-aldol.

Aldehydo aldol benzoate, $OBz\cdot CHMe\cdot CH_2\cdot CH{<}^{O}_{O}{>}CHMe$, is prepared by heating ether, acetaldehyde, and benzoic chloride with metallic sodium in a reflux apparatus, from which air is excluded by means of a current of hydrogen; after 24 hours, the ethereal liquid is treated successively with water and dilute potash, being finally dried with calcium chloride, and allowed to evaporate. The substance crystallises from petroleum in colourless, transparent prisms, and melts at 86—87°; when heated with water in sealed tubes at 100°, benzoic acid, aldol, and acetaldehyde are produced, whilst distillation gives rise to benzoic acid, crotonaldehyde, and acetaldehyde. Although insoluble in cold, dilute caustic potash, it dissolves on heating the liquid, which then becomes yellow owing to the production of aldehyde-resin; the substance is indifferent towards bromine, phenylhydrazine, and cold, aqueous potassium permanganate.

The production of a benzoate by the action of sodium on acetaldehyde in presence of benzoic chloride may be explained in two ways—either aldehyde, under the influence of sodium, is condensed to aldol, the sodium derivative of which is then produced, and combines with benzoic chloride, or the sodium derivative of acetaldehyde is first produced, undergoing condensation with more aldehyde to form the sodium derivative of aldehydo-aldol, which yields the benzoate in presence of benzoic chloride. The latter explanation is the more probable, owing to the fact that the action of sodium on aldol gives rise to a derivative which is not identical with the initial product of the action of the metal on acetaldehyde.

As the syrup from which aldehydo-aldol benzoate separates in the first instance undergoes decomposition when kept, depositing benzoic acid, it must be examined without delay. A solution of bromide in chloroform acts on it immediately, without liberating

hydrogen bromide, and benzoic acid is formed, along with an oily substance containing bromine; phenylhydrazine gives rise to benzophenylhydrazide, and a resinous phenylhydrazone; the readiness with which hydrolysis takes place suggesting the presence of an oxygen ether (compare Nef, Abstr., 1893, i, 629), which is probably aldol benzoate. This view is confirmed by the fact that the original syrup, when distilled, yields benzoic and crotonic acids, acetaldehyde, crotonaldehyde, and a small quantity of isocrotonaldehyde; moreover, when sodium acts on aldol in presence of benzoic chloride, hydrogen is liberated, and the oily product is identical with the syrup which remains after separating aldehydo-aldol benzoate. M. O. F.

Action of Aqueous Potassium Hydroxide and Carbonate on Isobutaldehyde. By MAXIMILIAN BRAUCHBAR (*Monatsh.*, 1896, **17**, 637—647. Compare Fossek, Abstr., 1882, 1279, and especially Franke, Abstr., 1896, i, 404.)—When isobutaldehyde is allowed to remain for 2 weeks in a closed vessel at the ordinary temperature, in contact with an equal volume of aqueous potassium hydroxide (containing 92 grams KOH per litre), it is largely converted into di-isobutaldehyde, some isobutyric acid being also formed. If the mixture is allowed to remain for 5 weeks, the main product is Fossek's "di-isopropylglycol," melting at 52°, but some di-isobutaldehyde is still obtained; the glycol is formed from the di-isobutaldehyde, a part of which is reduced to the glycol at the expense of another part, which becomes oxidised to isobutyric acid. Di-isobutaldehyde may be obtained unmixed with other substances, and in much better yield, by using potassium carbonate instead of the hydroxide; isobutaldehyde is allowed to remain for six weeks in contact with an equal volume of a saturated solution of the carbonate.

Di-isobutaldehyde is obtained as a liquid, but it crystallises when kept, and then melts at 90—92°. At 218°, its vapour is completely dissociated into that of isobutaldehyde; as a consequence of this easy dissociation, it is largely decomposed when distilled, even under diminished pressure; it boils between 90° and 120° under a pressure of about 16 mm. It yields a *monacetyl derivative* as a pale yellowish oil boiling at 136—139° under 18 mm. pressure; also a *monoxime* as a colourless, viscid oil boiling at 140° under 16 mm. pressure. It is reduced by sodium amalgam and dilute sulphuric acid to di-isopropyl glycol $CHMe_2\cdot CH(OH)\cdot CMe_2\cdot CH_2\cdot OH$, and oxidation with permanganate converts it into Fossek's acid,

$$C_8H_{16}O_3[=CHMe_2\cdot CH(OH)\cdot CMe_2\cdot COOH],$$

melting at 92°, together with some di-isopropyl ketone. These reactions of di-isobutaldehyde lead to the adoption of the formula

$$CHMe_2\cdot CH(OH)\cdot CMe_2\cdot CHO$$

for it; it is formed from isobutaldehyde by an aldol condensation.

C. F. B.

Action of Alcoholic Soda on Isobutaldehyde. By ADOLF FRANKE (*Monatsh.*, 1896, **17**, 672—676).—Contrary to Urbain's statement (Abstr, 1896, i, 590), isobutaldehyde, when heated with 5 per cent. alcoholic soda without cooling, yields a glycol,

$$CHMe_2\cdot CH(OH)\cdot CMe_2\cdot CH_2\cdot OH,$$

but not one of the three products he enumerates. At $-20°$, the product is di-isobutaldehyde (compare Brauchbar, preceding abstract); the oxime of this substance, when heated with acetic anhydride for 9 hours at 120°, yields the *acetyl* derivative of a *nitrile*,

$$CHMe_2\cdot CH(OAc)\cdot CMe_2\cdot CN,$$

as an oil which boils at 112° under 16 mm. pressure, and yields the acid, $CHMe_2\cdot CH(OH)\cdot CMe_2\cdot COOH$, when hydrolysed with aqueous potash.

C. F. B.

Hydrazidoacetic Acid. By WILHELM TRAUBE and E. HOFFA (*Ber.*, 1896, **29**, 2729—2730)—Isonitraminacetic acid, on reduction with sodium amalgam at 0° in slightly acid solution, yields hydrazidoacetic acid; this cannot be separated in the ordinary way by extraction with benzaldehyde, but on employing salicylaldehyde in its place, the condensation product readily separates as a white, crystalline precipitate. This orthohydroxybenzylidenehydrazido-acetic acid is, when pure, a colourless compound, becoming, however, brown when exposed to the air; it is readily soluble in alcohol and ether. It exists in two stereoisomeric forms, melting at 78° and 105° respectively. On removal of salicylaldehyde, free *hydrazidoacetic acid* is produced, forming colourless crystals, melting at 145°. It is very soluble in water, scarcely soluble in alcohol and ether. The *hydroiodide*, $NH_2\cdot NH\cdot CH_2\cdot COOH,HI$, melts at 156°.

J. F. T.

Electrolysis of Potassium Xanthate in Aqueous Solution. By J. F. CARL SCHALL (*Chem. Centr.*, 1896, i, 588; from *Zeits. Elektrotechn. u. Elektrochemie*, **2**, 475—476.)—By the electrolysis of potassium xanthate in concentrated aqueous solution, *ethylic bis-dithiocarbonate*, $S_2(CS\cdot OEt)_2$, is formed by the union of the anions $EtO\cdot CSS$. It separates at first as a yellow oil, which subsequently solidifies to a crystalline mass. The process is analogous to the formation of acetyl and benzoyl bisulphides by the electrolysis of the potassium salts of thioacetic and thiobenzoic acids respectively, as observed by Bunge (*Ber.*, 1870, **3**, 297).

E. W. W.

Methylenecarbamide. By BERNHARD TOLLENS (*Ber.*, 1896, **29**, 2751—2752).—Goldschmidt, in a recent paper on the action of formaldehyde on carbamide (this vol., i, 22) has omitted to refer to the papers of Hölzer (*Ber.*, **17**, 659; **18**, 3302), and Lüdy (Abstr., 1889, 1059), on the same subject.

A. H.

Asymmetric Nitrogen, V. Imides of Tartaric Acid and of Benzoyltartaric Acid. By ALBERT LADENBURG (*Ber.*, 1896, **29**, 2710—2719).—Further facts are brought forward in support of the theory of the asymmetric nitrogen atom. The two benzylmalimides of Giustiniani can either be structural- or stereo-isomerides. The former supposition seems improbable, from the fact that such isomerism has never as yet been observed in the case of inactive acids. Preparations of the imides of dibasic acids, such as succinic acid, inactive malic acid, meso-tartaric acid, and racemic acid showed that they existed in one form only. The occurrence of two isomeric benzylmalimides is, then, a further instance in support of the theory of the asymmetric nitrogen atom,

and can be explained in the same way as in the case of isoconiine. Other substituted malimides are in the course of investigation.

Substituted imides of tartaric acid are best prepared by heating the bitartrate of a primary amine above its melting point.

Tartarmethylimide, $\begin{matrix} OH\cdot CH\cdot CO \\ | \\ OH\cdot CH\cdot CO \end{matrix}\!\!>\!NMe$, from the bitartrate of methylamine (m.p. 170°), crystallises from alcohol in colourless, rhombic needles, melts at 178°, and has a rotation $[\alpha]_D = 193\cdot69°$. A second substance of the same composition is obtained on evaporating the mother liquor; this melts at 152°—153°, but was subsequently found to be a mixture of the methylimides of *d*- and *r*-tartaric acid, and not an homogeneous substance.

Tartarethylimide, $\begin{matrix} OH\cdot CH\cdot CO \\ | \\ OH\cdot CH\cdot CO \end{matrix}\!\!>\!NEt$, prepared in the same way as the methylimide, melts at 171—174°, and has a rotation of $[\alpha]_D =$ 165—166°.

The corresponding derivatives of benzoyltartaric acid are prepared by the action of benzoic chloride on the tartarimide. By the action of benzoic chloride on tartarmethylimide, only a very small quantity of the mono-benzoyl compound is produced, the chief product being *dibenzoyltartarmethylimide*, which crystalllies from alcohol in colourless prisms containing alcohol of crystallisation, and having the formula $4C_{19}H_{15}NO_6,3C_2H_6O$; it melts at 68°. On heating, the alcohol is rapidly given off, and two isomeric compounds are formed, the proportions of which depend on the temperature of decomposition. On heating at 100° for 1—2 hours, *α-dibenzoyltartarmethylimide* is produced, melting at 56°, and this, at the ordinary temperature, passes slowly into the β-compound.

β-Dibenzoyltartarmethylimide is best formed by heating the compound containing alcohol of crystallisation at 60° for 6—10 hours; it melts at 106°—107°, and at that temperature passes into the α-compound. The optical rotation for the α-component is 183·9, and for the β- 188·8, the difference being only very slight. It is, therefore, highly probable that these compounds are stereo-isomerides, and their occurrence can only be explained by the assumption of an asymmetric nitrogen atom.

The author concludes with a brief summary of his ideas as to the nature and function of the asymmetric nitrogen atom. He no longer supposes that it is possible to obtain optically active nitrogen compounds containing no asymmetric carbon atom, but understands by an asymmetric nitrogen atom, an atom serving to modify the activity produced by the asymmetric carbon atom, as is seen in the cases of isoconiine, the benzylmalimides and the dibenzoyltartarmethylimides. He further defines an asymmetric nitrogen atom as such that two of its valencies must form a ring compound, whilst the third is otherwise combined. Such a ring must, however, possess neither symmetry nor pseudo-symmetry, and must, therefore, be optically active. The capability of the third nitrogen bond to take up two, and perhaps in many rings four positions of equilibrium, causes stereoisomerism.

J. F. T.

Imides of Racemic Acid. By HERMANN WENDE (*Ber.*, 1896, **29**, 2719—2721).—The imides of racemic acid are prepared by heating the biracemate of the corresponding alkylamine above its melting point. The *methylimide* from *methylamine biracemate* (m.p. 180°) melts at 157—158°, and crystallises from alcohol in lustrous needles. *Ethylamine biracemate* melts at 142—143°, and, on heating, passes into the *ethylamide*, melting at 179°. The *propylamine* salt melts at 147°, and the *propylimide* crystallises in glistening needles. *Aniline biracemate* separates when molecular quantities of racemic acid and aniline are mixed; the crystals contain 1 mol. H_2O and melt and decompose at 173°; the *phenylimide* melts at 235—236°. Benzylamine biracemate melts at 178°. The *benzylimide* formed from this crystallises from glacial acetic acid in leaflets melting at 168°. J. F. T.

Ethereal Phosphopalladates and their Ammoniacal Derivatives. By E. FINCK (*Compt. rend.*, 1896, **123**, 603—604).—*Ethylic phosphopalladate*, $P_2(OEt)_6PdCl_2$, forms red, prismatic crystals, insoluble in water, but soluble in alcohol. It is obtained by placing phosphopalladic chloride and absolute alcohol in separate dishes under a bell jar, which also encloses a dish containing quick lime. *Methylic phosphopalladate* is strictly analogous to it in composition and is obtained in a similar way; it crystallises in white, prismatic needles, soluble in alcohol, benzene, and ether.

When treated with ammonia in presence of water or benzene, ethylic phosphopalladite yields colourless crystals of the composition

$$P(OEt)_3PdCl_2,2NH_3,$$

whilst in presence of alcohol the product is $P(OEt)_3PdN_2H_4,2HCl + P(OEt)_3NH_3PdN_2H_4,2HCl$. The methyl derivative yields analogous compounds under the same conditions.

Ethylic phosphopalladate, when evaporated with aqueous ammonia, yields white, deliquescent crystals of the compound

$$P_2O(OEt)_5PdNH_2,HCl,$$

whilst the methyl derivative yields the compound

$$P_2(OMe)_6N_2H_4,2HCl\ [?\ P_2(OMe)_6PdN_2H_4,2HCl].$$

When heated with paratoluidine and alcohol, ethylic phosphopalladite yields white, prismatic crystals of the compound $P(EtO)_3C_7H_9N,PdCl_2$; an analogous methyl derivative is obtained in the same way. Pyridine, under similar conditions, yields the compounds

$$P(OEt)_3C_5NH_5,PdCl_2 \text{ and } P(OMe)_3C_5NH_5,PdCl_2.$$

C. H. B.

Constitution of Vinaconic [Trimethylenedicarboxylic] Acid. By RICHARD MARBURG (*Annalen*, 1896, **294**, 89—134. Compare Abstr., 1895, i, 171).—The main facts which lead the author to support the view of W. H. Perkin, jun., who regards vinaconic acid as trimethylenedicarboxylic acid, have been already described (*loc. cit.*); the present paper contains an amplified record of the experimental details.

Ethylic γ-chlorisosuccinate, $CH_2Cl\cdot CH_2\cdot CMe(COOEt)_2$, obtained from ethylic sodioisosuccinate and ethylenic chloride, boils at 127—128° under a pressure of 9 mm.; not more than 10 per cen . of this salt is produced, and a certain amount of ethylic symmetrical α-dimethyl-

adipindicarboxylate [hexane-2 : 2 : 4 : 4-tetracarboxylate] is also formed (compare Abstr., 1894, i, 441.) When ethylic γ-chlorisosuccinate is heated at 260—270°, it yields ethylic α-methylbutyrolactonecarboxylate (compare Abstr., 1895, i, 171). The *barium* salt of α-methylbutyrolactonecarboxylic acid contains $4H_2O$, the *calcium* salt, $1H_2O$, whilst the *silver* salt is anhydrous. *Barium* hydroxyethylisosuccinate contains $3H_2O$, and the *silver* salt crystallises from water.

α-Methylbutyrolactone is obtained on heating the lactonecarboxylic acid at 140°, carbonic anhydride being eliminated; this substance is also produced on hydrolysing γ-phenoxyethyl-α-methylacetic acid (Trans., 1896, 173). The *barium, calcium,* and *silver* salts of α-methyl-γ-hydroxybutyric acid are anhydrous.

Methylvinaconic (*1-methyltrimethylene-2 : 2-dicarboxylic*) *acid*,

$$\begin{matrix} CHMe \diagdown \\ | \qquad\quad C(COOH)_2, \\ CH_2 \diagup \end{matrix}$$

the ethylic salt of which is produced when ethylic sodiomalonate is treated with propylenic bromide (Abstr., 1895, i, 172), crystallises from benzene in lustrous needles, and melts at 113·5°; the *barium* salt contains $2H_2O$, the *hydrogen barium* salt $3H_2O$, and the *calcium* salt $5H_2O$, whilst the *silver* and *hydrogen silver* salts are anhydrous, and crystallise from water. Methylvinaconic acid is quite distinct from allylmalonic acid.

γ-*Bromopropylmalonic acid*, $CHMeBr \cdot CH_2 \cdot CH(COOH)_2$, is obtained by the action of hydrobromic acid on methylvinaconic acid, and when crystallised from chloroform, melts at 107·5°; it is identical with the acid produced on treating allylmalonic acid with the same agent, and boiling water converts it into the γ-methyl-α-butyrolactonecarboxylic (valerolactonecarboxylic) acid, obtained by Hjelt from the hydrogen bromide additive compound of allylmalonic acid.

The *bromine additive compound* of methylvinaconic acid,

$$C_4H_6Br_2(COOH)_2,$$

crystallises from chloroform in needles, and melts and decomposes at 130—131°; the bromine additive compound of allylmalonic acid melts at 124·5°. Methylvinaconic acid is very readily attacked by concentrated nitric acid, and after 10—20 hours two molecular proportions of carbonic anhydride are eliminated; vinaconic acid, on the other hand, yields no gas during the first 5 days, the quantity eliminated after 20 days representing less than a tenth part of one molecular proportion.

1 : 2-*Methyltrimethylenecarboxylic acid*, $\begin{matrix} CHMe \diagdown \\ | \qquad\quad CH \cdot COOH, \\ CH_2 \diagup \end{matrix}$ is obtained along with valerolactone on submitting methylvinaconic acid to dry distillation above 140°; it is a colourless, limpid liquid, having the odour of butyric acid, and boils at 190—191° under a pressure of 745 mm. It remains liquid at −18°, and has the sp. gr. = 1·030 at 0°/4° and 1·015 at 18°/4°. The *calcium* salt contains $1\frac{1}{2}H_2O$, the *barium* salt $2H_2O$; the *silver* salt is also crystalline. Methyltrimethylenecarboxylic acid is distinct from ethylidenepropionic and allylacetic acids.

M. O. F.

Mesitylene from Acetone. By VICTOR MEYER and W. MOLZ (*Ber.*, 1896, **29**, 2831—2833). (Compare Abstr., 1896, i, 547.)—The fractions of mesitylene of high-boiling point prepared from acetone do not yield any appreciable quantity of monoketones when treated with acetic chloride and aluminium chloride; it is improbable, therefore, that they contain hemimellithene. The observation made by Lucas and Sohn that a small quantity of hemimellithenecarboxylic acid is produced by the carboxylation of mesitylene, is doubtless to be explained by the occurrence of isomeric change similar to that which obtains when symmetrical durene is treated in the same way.

A. L.

Constitution of the Nitroso-derivatives of the Two Secondary Ethylidenanilines. By ALEXANDER EIBNER (*Ber.*, 1896, **29**, 2977—2981).—The two isomeric ethylidenanilines described by von Miller and Plöchl (Abstr., 1894, i, 410) both yield nitroso-derivatives, which are sulphur-yellow powders, soluble in hot alcohol and in benzenes; on the addition of ether to these solutions, the compounds are obtained in bright yellow, glistening crystals. The nitroso-compound from the base obtained by Eckstein melts at 161°, and is sparingly soluble in hot alcohol, but insoluble in ether; that from the author's base melts at 120°, is readily soluble in hot alcohol and only sparingly so in ether.

Both compounds, when reduced with tin and hydrochloric acid, yield the same products, namely, tetrahydroquinaldine and paraphenylenediamine. This reaction agrees with the formula

$$NO{\cdot}NPh{\cdot}CHMe{\cdot}CH_2{\cdot}CH{:}N{\cdot}C_6H_4{\cdot}NO \quad [N:NO=1:4]$$

for the two nitroso-compounds.

On adding ferric chloride to a solution of the hydrochlorides of tetrahydroquinaldine and paraphenylenediamene in molecular proportion, a beautiful green coloration is produced, which turns to blue on the addition of water.

Other secondary Schiff's bases can yield similar nitroso-compounds—for example, Sender's propylidenaniline (Abstr., 1892, 1189) and the base from orthotoluidine and acetaldehyde.

J. J. S.

Orthophenylenebiguanide. By RUDOLF ZIEGELBAUER (*Monatsh.*, 1896, **17**, 648—666).—Monamines, NH_2R or NHR_2, simply combine with dicyanodiamide, $C_2H_4N_4$, yielding substituted biguanides, $C_2H_6RN_5$ or $C_2H_5R_2N_5$. Orthophenylenediamine hydrochloride, however, when it is heated with dicyanodiamide, in molecular proportion, in alcoholic solution for 7 hours at 105°, reacts with evolution of ammonia. The product formed, however, has still the properties of a biguanide, and the constitution $C_6H_4{<}{\begin{smallmatrix}NH\cdot C(NH)\\ NH\cdot C(NH)\end{smallmatrix}}{>}NH$ must be assigned to it. The author concludes that this and other reactions of dicyanodiamide are best explained by adopting the formula $CN{\cdot}NH{\cdot}C(NH){\cdot}NH_2$ for that substance.

Orthophenylenebiguanide, $C_8H_9N_5,H_2O$, crystallises in yellowish, nacreous plates, and melts and decomposes at 242° (uncorr.). The following salts were prepared: *nitrate*, $(C_8H_9N_5)_3,5HNO_3 + 3H_2O$ ($\frac{9}{10}$ths of the nitric acid can be titrated with baryta); *hydrochloride*, $C_8H_9N_5,HCl$; *platinochloride*, $C_8H_9N_5,PtCl_4 + 2H_2O$, orange-yellow, darkens above

260°, but is still unmelted at 300°; *sulphates*, $C_8H_9N_5,H_2SO_4+4H_2O$ and $(C_8H_9N_5)_2,H_2SO_4+H_2O$, the latter brownish in colour; *chromate*, $C_8H_9N_5,H_2Cr_2O_4$, yellow; *ferrocyanide* $(C_8H_9N_5)_2,H_4FeC_6N_6+3H_2O)$, yellowish. A red *cobalt* and a chocolate-brown *nickel* derivative, $(C_8H_8N_5)_3Co+3\frac{1}{2}H_2O$ and $(C_8H_8N_5)_2Ni$, were also prepared; such metallic derivatives are obtained by mixing a solution of a salt of the biguanide with a salt of the metal in question, pouring the mixture into a large quantity of hot, dilute alkali hydroxide, and allowing the whole to cool. C. F. B.

Reduction Products from Azo-compounds. By PAUL JACOBSON, M. JAENICKE and FRIEDRICH MEYER (*Ber.*, 1896, **29**, 2680—2690). —The reduction of benzene azoanisoïl, $OMe\cdot C_6H_4\cdot N_2Ph$, and benzeneazoveratrole, $C_6H_4(OMe)_2\cdot N_2Ph$ [$(OMe)_2=3:4$], have been studied, only ethylic ethers having been previously examined. The reduction and subsequent operations were carried out just as in the case of benzeneazophenetoïl (Abstr., 1896, i, 23). Benzeneazoanisoïl behaves like the last substance, yielding the ortho- and para-semidine bases,

$$OMe\cdot C_6H_3(NH_2)\cdot NHPh\ [OMe:NH_2:NHPh=1:4:3]$$
$$\text{and } OMe\cdot C_6H_4\cdot NH\cdot C_6H_4\cdot NH_2,$$

in addition to the bases anisidine and aniline, which result from a division of the molecule; the quantitative relations are also similar. Benzeneazoveratrole also undergoes a similar reduction, but the action could not be studied quantitatively, for the main reaction is accompanied by another, which results in the removal of one methoxyl group, and the formation of a benzidine base,

$$NH_2\cdot C_6H_3(OMe)\cdot C_6H_4\cdot NH_2.$$

2-*Amido*-5-*methoxydiphenylamine* (orthosemidine base) melts at 73°, and yields a *carbon bisulphide* derivative, $C_{14}H_{12}N_2SO$, melting at 208°; a yellow *salicylidene* derivative, $C_{20}H_{18}N_2O_2$, melting at 132° and oxidised by mercuric oxide to a *salicylic* derivative, $C_{20}H_{16}N_2O_2$, melting at 123°; with formic acid, a *methenyl* derivative,

$$OMe\cdot C_6H_3{<}{}^{\text{—N—}}_{\text{NPh}}{>}CH,$$

melting at 77°; and with benzil, a *stilbazonium base*,

$$OMe\cdot C_6H_3{<}\begin{matrix}N\text{=====}CPh\\ \mid\\ NPh(OH)\cdot CPh\end{matrix},$$

melting at 163—165°. 4-*Amido*-4'-*methoxydiphenylamine* (parasemidine base) melts at 102°.

Benzeneazoveratrole was prepared from crystallised guaiacol by diazotising the latter, and boiling the sodium salt of the product, benzeneazoguaiacol, with alcoholic methylic iodide; it is red, and melts at 44·5—45°. 2-*Amido*-4:5-*dimethoxydiphenylamine* (orthosemidine base) has a pale violet colour, and melts at 151°; its *methenyl derivative* melts at 106—107°. 4:4'-*Diamido*-2-*methoxydiphenyl* (benzidine base), is pale pink, and melts at 104°. Incidentally, the *acetyl* derivative of amidoveratrole, $C_6H_3(OMe)_2\cdot NHAc$, was prepared; it is silver-grey, and melts at 132·5—133°.

Guaiacoldis-azobenzene, $OMe\cdot C_6H_2(OH)(N_2Ph)_2$, is obtained at the same time as benzene-azoveratrole; it is dark grey with a violet sheen,

and melts at 150—155°. *Benzeneazoguaiacol*, obtained as mentioned above, forms red prisms, melting at 70·5—71·5° C. F. B.

Uramides, Urethanes, and Oxamethanes of Paraphenylenediamine and Metaphenylenediamine. By HUGO SCHIFF and ADRIANO OSTROGOVICH (*Annalen*, 1896, **293**, 371—388. Compare Abstr., 1894, i, 236, 333).—The derivatives of paraphenylenediamine have been already described (*loc. cit.*), and the paper contains a tabular representation of their relationship; a description of the metaphenylenediamine derivatives appears for the first time.

Acetylmetaphenylenediamine *hydrochloride*, $HCl,NH_2\cdot C_6H_4\cdot NHAc$, is obtained by heating metaphenylenediamine dihydrochloride and sodium acetate in molecular proportion with water; it forms a reddish, crystalline mass, having no definite melting point, and softens at 194°.

Metacetamidophenylcarbamide, $NHAc\cdot C_6H_4\cdot NH\cdot CONH_2$, is produced on mixing cold, concentrated, aqueous solutions of acetylmetaphenylenediamine hydrochloride and potassium cyanate; it crystallises in reddish needles, and melts at 225°. Metaphenylenecarbamide, $C_6H_4{<}{\substack{NH\\NH}}{>}CO$, is also produced in small quantity, and the same substance is obtained when acetamidophenylcarbamide is submitted to frequent recrystallisation.

Metamidophenylcarbamide hydrochloride, $HCl,NH_2\cdot C_6H_4\cdot NH\cdot CO\cdot NH_2$, is formed when a very concentrated solution of acetamidophenylcarbamide is boiled with hydrochloric acid for 10 minutes; it crystallises from dilute alcohol in lustrous scales, and melts at 281—282°

Metamidophenyloxamic acid, $NH_2\cdot C_6H_4\cdot NH\cdot CO\cdot COOH$, has been already described by Klusemann (this Journal, 1875, 269) and melts at 225°; the *hydrochloride* crystallises in needles and decomposes above 300°, whilst the *potassium* salt crystallises in yellow scales, and decomposes about 270°. The *acetyl* derivative melts at 125°, and begins to decompose at 130°. *Uramidophenyloxamic acid*,

$$NH_2\cdot CO\cdot NH\cdot C_6H_4\cdot NH\cdot CO\cdot COOH,$$

is obtained by heating potassium amidophenyloxamate with carbamide at 130°, and also from amidophenyloxamic acid and potassium cyanate; it crystallises from water in small needles, and melts at 230°.

Metaphenylenedioxamic acid, $C_6H_4(NH\cdot CO\cdot COOH)_2$, is obtained by heating alcoholic acetylmetaphenylenediamine with ethylic oxalate in a reflux apparatus; it separates from alcohol in crystalline aggregates, and melts, decomposing, at 240°. M. O. F.

βγ-Substituted Derivatives of Hydantoin. By ENRICO QUENDA (*Chem. Centr.*, 1896, i, 701; from *Ann. Chim. Farm.*, **23**, 61—64). —Methylglycocine and monoparatolylcarbamide, when heated at 135—140°, yield diparatolylcarbamide and *γ-paratolyl-β-methylhydantoin*, the former being insoluble in water. The latter, which gives Weyl's reaction, melts at 112—113°, is soluble in water, and easily so in alcohol. Similarly, monorthotolylcarbamide and methyl-glycocine form diorthotolylcarbamide, which melts at 250°, and *γ-orthotolyl-β-methylhydantoin*. The latter, which was neither obtained in a crystalline form, nor analysed, does not give Weyl's reaction. E. W. W.

Derivatives of Paramidophenol. By VICTOR WIRTHS (*Arch. Pharm.*, 1896, **234**, 620—634.)—The entry of a dibasic acid radicle into the amido-group of an amidophenol may be effected by heating the latter with an acid anhydride or amide in an oil-bath or over a free flame. Phthalylparamidophenol has already been obtained by this method (Piutti, Abstr., 1886, 1026).

Succinylparamidophenol, $OH\cdot C_6H_4\cdot N\dot{:}(CO)_2\dot{:}C_2H_4$, from succinic anhydride and paramidophenol, crystallises in needles, melts at 270°, and is insoluble in all the usual solvents, except alcohol and glacial acetic acid. *Oxalylparamidophenol*, $OH\cdot C_6H_4\cdot N<\begin{matrix}CO\\|\\CO\end{matrix}$, may be prepared by heating either oxalic acid or oxamide with paramidophenol; it crystallises in needles, does not melt at 350°, and sublimes when sharply heated, being at the same time partly decomposed.

The derivatives under consideration can also be prepared by heating paramidophenol with ethereal salts in a sealed tube at 160°. The foregoing oxalyl derivative has been obtained in this way. With diethylic tartrate, 2 molecules of amidophenol enter into the reaction, yielding *tartronyldiparamidophenol*,

$$OH\cdot C_6H_4\cdot NH\cdot CO\cdot CH(OH)\cdot CH(OH)\cdot CO\cdot NH\cdot C_6H_4\cdot OH,$$

which crystallises in reddish needles, melts and decomposes at 282°, and dissolves in glacial acetic acid and alcohol.

Succinylparanisidine, $OMe\cdot C_6H_4\cdot N\dot{:}(CO)_2\dot{:}C_2H_4$, prepared by melting succinic anhydride with anisidine, crystallises in needles, melts at 162°, and dissolves in hot water and alcohol. Succinylparaphenetidine melts at 158° (Piutti, *Chem. Zeit.*, 1896, **20**, 54). *Succinyldiparaphenetidine*, $OEt\cdot C_6H_4\cdot NH\cdot CO\cdot C_2H_4\cdot CO\cdot NH\cdot C_6H_4\cdot OEt$, crystallises in needles, melts at 258°, and is insoluble in water.

By heating anisidine or phenetidine with ethereal salts in tubes at 150—160°, the following have been prepared.

Oxalylparanisidine, $OMe\cdot C_6H_4\cdot N<\begin{matrix}CO\\|\\CO\end{matrix}$, which crystallises in needles, melts at 115°, and dissolves in water and alcohol. *Oxalyldiparanisidine*, $C_2O_2(NH\cdot C_6H_4\cdot OMe)_2$, crystallises in needles, melts at 260°, and is insoluble in water. *Oxalylparaphenetidine* crystallises in six-sided tablets, melts at 110°, and dissolves in hot water, alcohol, and glacial acetic acid. *Tartronyldiparanisidine* crystallises in large, lustrous laminæ, melts at 259°, and dissolves freely in alcohol and hot glacial acetic acid, but only sparingly in ether, chloroform, and benzene. *Tartronyldiparaphenetidine* forms large laminæ, melts at 271°, and resembles the preceding compound in solubility.

By heating such substituted amidophenols as have been described above with acid chlorides, compounds containing acid radicles substituted in the hydroxyl of the phenol are obtainable. The following instances are cited; the compounds are best crystallised from glacial acetic acid. *Phthalylparamidophenylic benzoate*,

$$OBz\cdot C_6H_4\cdot N\dot{:}(CO)_2\dot{:}C_6H_4;$$

needles, melting at 256°. *Phthalylparamidophenylic butyrate*; needles, melting at 156°. *Phthalylparamidophenylic propionate*; needles, melting at 158°. *Phthalylparamidophenylic acetate*; needles, melting at 226°.

Succinylparamidophenylic benzoate, $OBz\cdot C_6H_4\cdot N\colon(CO)_2\colon C_2H_4$; needles, melting at 215°. *Succinylparamidophenylic propionate*; needles, melting at 178°. A. G. B.

Action of Phthalic and Succinic Chlorides on Compounds of the Type R·NH₂. By BRONISLAW PAWLEWSKI (*Ber.*, 1896, **29**, 2679. Compare Abstr., 1895, i, 414).—By heating orthamidobenzoic acid with phthalic chloride, *phthalanilorthocarboxylic acid*, $CO<\substack{C_6H_4\\-O-}>C\colon N\cdot C_6H_4\cdot COOH$, is obtained; it melts and decomposes at 241—242°. Paranitraniline and succinic chloride yield pale yellowish *succinylparanitrophenylimide*, $\begin{matrix}CH_2\cdot CO\\ | \\ CH_2\cdot CO\end{matrix}>N\cdot C_6H_4\cdot NO_2$, melting at 175°. C. F. B.

Aromatic Chlorophosphines and their Derivatives. By C. A. AUGUST MICHAELIS (*Annalen*, 1896, **293**, 261—325; **294**, 1—55. Compare Abstr., 1894, i, 586; this vol., i, 49).—[With HUBERT GLAUBITZ.] —*Paratolylcyanophosphine*, $C_6H_4Me\cdot P(CN)_2$, obtained from paratolylchlorophosphine and silver cyanide, is a bright yellow, viscous liquid, which boils at 145° under a pressure of 50 mm.; *paratolylthiocyanophosphine*, $C_6H_4Me\cdot P(SCN)_2$, is a reddish-yellow liquid, which boils at 237—240° under a pressure of 40 mm.

Phenylic paratolylphosphonate, $C_6H_4Me\cdot PO(OPh)_2$, is obtained from tolyloxychlorophosphine and phenol (2 mols.), the mixture being heated at 120—130°; it is a colourless, viscous liquid, which exhibits feeble, blue fluorescence, and boils above 360°. The *chloride*, $C_6H_4Me\cdot PO(OPh)Cl$, is produced when one-half the quantity of phenol is employed; it is a white, crystalline mass, which melts at 55°, and boils above 360° without undergoing decomposition. *Silver phenylic paratolylphosphonate* and *phenylic paratolylphosphonamide*, $C_6H_4Me\cdot PO(OPh)\cdot NH_2$, have also been prepared, and the latter substance crystallises from ether and melts at 115—116°. The *phenylhydrazide* of monophenylic paratolylphosphonate crystallises in small, white needles, and melts at 173—174°; the *piperidide* is a yellow oil.

Paratolylic paratolylphosphonate, $C_6H_4Me\cdot PO(O\cdot C_6H_4Me)_2$, is a viscous liquid which boils above 360°; the *chloride* melts at 60°, and boils above 360° without undergoing change.

Phenylenic paratolylphosphonate, $C_6H_4Me\cdot PO\colon O_2\colon C_6H_4$, melts at 81°, forming a feebly fluorescent liquid which boils above 360°; the *chloride* is a colourless, viscuous liquid, which does not decompose when distilled above 360°.

Paratolylphosphondiamide, $C_6H_4Me\cdot PO(NH_2)_2$, crystallises in colourless, lustrous leaflets, and melts at 176°; this substance is not formed when tolyloxychlorophosphine is treated with ammonium carbonate, a compound being produced which melts at 74°, and is probably an *isomeride* of paratolylphosphonic acid (m. p. 189°), as it yields this product when treated with boiling water. The *dianilide*, $C_6H_4Me\cdot PO(NHPh)_2$, crystallises in small, nacreous needles, and melts at 209°. The *toluidide* forms slender, snow-white needles, and melts at 237°, and the *monotoluidide*, $C_6H_4Me\cdot PO(OH)\cdot NH\cdot C_6H_4Me$, is a white powder which melts at 208°; the *phenylhydrazide* forms slender needles, and melts at 171°.

*Aniline-*n*-tolylphosphonic acid,* $C_6H_4Me{\cdot}PO(OH){\cdot}NHPh$, is obtained as chloride along with the foregoing anilide when tolyloxychlorophosphine is heated with aniline hydrochloride; it is a white powder, which melts at 150°, and is decomposed when dissolved in alcohol or glacial acetic acid. The *copper* salt is a bright blue powder; the *phenylic* salt melts at 59°, forming a very viscous, highly-refractive oil, which boils at 283° under a pressure of 48 mm.

[With E. PIPER.]—*Nitroparatolylphosphonic acid,*

$$NO_2{\cdot}C_6H_3Me{\cdot}PO(OH)_2,$$

is obtained by heating paratolylphosphonic acid with fuming nitric acid for 2 hours in a reflux apparatus; it crystallises in aggregates of pale yellow needles, and melts at 191°. The *barium* salt forms yellowish leaflets, and contains $2H_2O$, and the *calcium* salt contains $1H_2O$; the *lead*, *copper*, and *silver* salts are anhydrous, and the *ethylic* salt is liquid.

Dinitroparatolylphosphonic acid is obtained by heating the phosphonic acid with a mixture of concentrated and fuming nitric acids for 3 hours on the water bath; it crystallises from water in yellowish leaflets, and melts at 251°. The *barium* salt contains $2H_2O$, and the *lead* salt is anhydrous.

Amidoparatolylphosphonic acid is formed on reducing the nitroderivative with tin and hydrochloric acid, and crystallises from alcohol in lustrous needles; it rapidly darkens in the atmosphere, and melts indefinitely at 270—290°. The *silver* and *lead* salts are amorphous, and the *ethylic* salt is a yellow liquid. The action of nitrous acid in presence of hydrochloric acid gives rise ultimately to trichlorotoluquinone, along with a substance which is probably tartronic acid.

Parabenzophosphonic acid, $COOH{\cdot}C_6H_4{\cdot}PO(OH)_2$, was obtained by Michaelis and Paneck on oxidising paratolylphosphonic acid with potassium permanganate. The *hydrogen calcium* and *hydrogen barium* salts are anhydrous, and the *copper* salt is a bright blue, crystalline substance, containing $1\frac{1}{2}H_2O$. The *dihydrogen ethylic* salt crystallises in long, colourless needles, and melts at 78°; the *hydrogen silver ethylic* salt forms snow-white crystals. The *monamide* crystallises in small needles, melting above 300°, and forms the *silver* salt, which is a white powder very sensitive to light. The *anilide* separates from alcohol in small, white crystals, and melts at 242°.

[With MORITZ G. MIETHING.]—*Paratolyldimethylphosphine oxide,* $C_6H_4Me{\cdot}PMe_2O$, is obtained by suspending paratolyldimethylphosphine (Czimatis, Abstr., 1883, 57) in much water, and adding a slight excess of mercuric oxide; it is a hygroscopic, crystalline mass, and melts at 95°. The *nitro*-derivative forms yellow prisms, melting at 175°, and yields a *mercurichloride,* which crystallises from water in slender, white needles, and melts at 127°.

Dimethylphosphine-oxide-parabenzoic acid, $COOH{\cdot}C_6H_4{\cdot}PMe_2O$, is produced on oxidising paratolyldimethylphosphine oxide with potassium permanganate; it separates from alcohol and ether in colourless crystals, melts at 240°, and boils above 360° under a pressure of 15 mm. The *mercurichloride* crystallises in beautiful white needles, and melts at 154°, the *aurochloride* forms colourless, rhombic plates, and the *platinochloride* crystallises in colourless plates, and melts at 234°. The *ammonium* salt melts and decomposes at 212°, the *silver* salt forms

colourless crystals, and the *copper* salt is a bluish-green powder. The *chloride* is a liquid, and, when treated with aniline, yields the *anilide*, which crystallises from alcohol in nacreous leaflets, and melts at 235°.

Tolyldimethylphosphobetaïne, $C_6H_4Me\cdot PMe_2<^{CH_2}_{-O-}>CO$, is obtained by the action of silver oxide on the *hydrochloride* of the ethylic salt, $C_6H_4Me\cdot PMe_2Cl\cdot CH_2\cdot COOEt$, which is formed by the action of ethylic chloracetate on tolyldimethylphosphine, separating as a hygroscopic crystalline powder, which melts at 153°; the *platinochloride* of the ethylic salt forms slender, yellowish-red needles, and melts at 200°. The *betaïne* itself melts at 206°, and the *hydrochloride* at 172°, whilst the *platinochloride* crystallises from hot water in small needles, and melts at 220°.

Tolyldiethylphosphine oxide, $C_6H_4Me\cdot PEt_2O$, forms hygroscopic crystals, and melts at 74°; the *mercurichloride* contains $1H_2O$, and melts at 135°. The *nitro*-derivative is an oil, forming a *mercurichloride*, which melts at 105°.

Diethylphosphine-oxide-parabenzoic acid, $COOH\cdot C_6H_4\cdot PEt_2O$, is an oil which distils under a pressure of 15 mm. without undergoing change; the *anilide* crystallises in leaflets, and melts at 198°, and the *mercurichloride* at 134°. The *betaïne* is a hygroscopic mass, and yields a *platinochloride*, which crystallises from hot water in yellow needles, and melts at 157°; the *ethylic* salt of the betaïne is a liquid, forming the *hydrochloride*, which melts at 96°.

[With Luis da Rocha Schmidt.]—Orthotolylchlorophosphine is a colourless, highly-refractive liquid, having a sp. gr. = 1·3067 at 18·5°, and boils at 244°.

Orthotolyltetrachlorophosphine, $C_6H_4Me\cdot PCl_4$, is a white, crystalline substance, and melts at 63—66°. *Orthotolyloxychlorophosphine*,

$$C_6H_4Me\cdot POCl_2,$$

is obtained from the tetrachloride by means of sulphurous anhydride, and forms a colourless liquid having a sp. gr. = 1·3877 at 18·5°, and boils at 273°.

Orthotolylphosphine oxide, $C_6H_4Me\cdot PO_2$, crystallises from benzene in short prisms. *Ammonium* orthotolylphosphinite is a crystalline salt, becoming brown on exposure to air, and the *barium* salt contains $1H_2O$; the *copper* and *lead* salts are anhydrous, and the *anilide* crystallises in white needles, and melts at 234°.

Chlororthotolylphosphonic acid [Me:P:Cl = 1:2:4] is produced by the action of chlorine on orthotolylphosphonic acid, and separates from dilute alcohol in small crystals, melting at 205°; the *silver* salt is amorphous. *Dichlororthotolylphosphonic acid* crystallises in slender needles, and melts at 240°; the *silver* salt is a white powder.

[With E. Piper.]—*Nitro-orthotolylphosphonic acid*,

$$[Me : P : NO_2 = 1 : 2 : 4],$$

is obtained more readily than the para-compound, being formed when a solution of the phosphonic acid in fuming nitric acid is evaporated on the water bath; it crystallises from water in pale yellow needles, and melts at 174°. The *barium* and *calcium* salts are anhydrous.

Amidorthotolylphosphonic acid, obtained by reducing the nitro-com-

pound, crystallises in needles which quickly become brown, and softens at 280—300°, above which temperature it decomposes; the *barium* salt is a reddish-brown powder, sparingly soluble in water, and the *calcium* salt is also moderately soluble.

Orthobenzophosphonic acid, obtained by oxidising orthotolylphosphonic acid with potassium permanganate, separates from water in small crystals, melting at 172°; when gently heated in small quantity, it sublimes for the most part without undergoing change. The *silver* salt is a white substance, which is sensitive to light; the *chloride* melts at 54°

Orthotolyldiethylphosphine, $C_6H_4Me\cdot PEt_2$, is a mobile, colourless liquid of penetrating odour, and boils at 263°. The *methiodide* crystallises from water in colourless needles, and melts at 98°; the *ethiodide* crystallises from alcohol, and melts at 162°.

[With WILLIAM BERGHEGGER.]—*Metatolylchlorophosphine* is prepared by heating small quantities of 1:3-mercuryditolyl (Abstr., 1895, i, 368) with phosphorus trichloride (10 parts) in sealed tubes at 200° for 12 hours; it is a dense, colourless liquid, which boils at 235°, and has a sp. gr. = 1·282 at 22°.

Metatolyltetrachlorophosphine is a viscous oil, which becomes crystalline below 0°. *Metatolyloxychlorophosphine* boils at 275°, and has a sp. gr. = 1·3533 at 18°.

Ammonium metatolylphosphinite crystallises in lustreless, white needles, and the *potassium* salt is deliquescent; the *barium* salt forms stellar aggregates of needles, and the *phenylhydrazine* salt, crystallising in yellow needles, melts and decomposes at 131°.

Metatolylphosphonic acid, $C_6H_4Me\cdot PO(OH)_2$, crystallises from water in lustreless, white needles, and melts at 116—117°. The *hydrogen potassium* salt forms white needles, and the *trihydrogen potassium* salt, white leaflets; the *barium*, *silver*, and *hydrogen silver* salts are anhydrous.

Chlorometatolylphosphonic acid [Me:P:Cl = 1:3:4] is formed when a stream of chlorine is passed into an aqueous solution of metatolylphosphonic acid for 20 minutes; it crystallises from water in small, white needles, and melts at 176°. The *silver* salt is a white powder, and resists the action of light. Trichlorotolylphosphonic acid

[Me:P:Cl_3 = 1:3:2:4:5],

is obtained by prolonged action of the halogen, and crystallises in needles or leaflets, melting at 220°; when heated above this temperature, it yields 1 : 2 : 4 : 5-trichlorotoluene, and is, therefore, identical with trichlorotolylphosphinic acid described by Michaelis and Lange (this Journal, 1876, i, 392).

Bromometatolylphosphonic acid [Me:P:Br = 1:3:4] crystallises from water in white needles, and melts at 198°; the *silver* salt is amorphous.

Metabenzophosphonic acid is obtained by oxidising metatolylphosphonic acid, and crystallises from alcohol in small, white needles, melting at 245—246°; the *silver*, *lead*, and *barium* salts are anhydrous, and the *chloride* is a white, crystalline substance, which melts at 61°, and boils at 360°.

[With MORITZ LEWSCHINSKY].—*Parethylphenylchlorophosphine* (*ethylbenzenechlorophosphine*), $C_6H_4Et\cdot PCl_2$, is prepared from ethylben-

zene, phosphorus trichloride and aluminium chloride, and forms a colourless, highly-refractive liquid, which boils at 250—252°, and has a sp. gr. = 1·227 at 17°.

Ethylbenzenetetrachlorophosphine is obtained by the action of chlorine on the foregoing substance, and forms a white, crystalline mass, melting at 51°. *Ethylbenzeneoxychlorophosphine* is a colourless liquid which boils at 294°, and has a sp. gr. = 1·29 at 16°.

Ethylbenzenephosphinous acid, $C_6H_4Et{\cdot}PHO{\cdot}OH$, is produced when the chlorophosphine is treated with water, and the liquid evaporated; it separates in crystals, and melts at 63—64°. The *ammonium* salt forms lustrous, quadratic leaflets, and the *barium* salt is a crystalline powder containing $1H_2O$; the copper salt is a bluish-green, crystalline powder, and the *phenylhydrazine* salt separates from hot water in lustrous, yellowish-white leaflets, and melts at 133°.

Ethylbenzenephosphonic acid crystallises from water in slender, lustrous needles, and melts at 164°; the *hydrogen ammonium* salt crystallises with difficulty, and the *hydrogen phenylhydrazine* and *trihydrogen potassium* salts crystallise from water. The *barium* salt forms lustrous needles, and contains $3H_2O$; the *copper* salt is greenish-white, and contains $1H_2O$, and the *silver* salt is a white, crystalline powder. Ethylbenzenephosphinic acid is immediately oxidised by potassium permanganate, in alkaline solution, yielding benzophosphinic acid, carbonic anhydride, and water.

Phosphino-ethylbenzene, $C_6H_4Et{\cdot}PO_2$, is obtained by dissolving ethylbenzene-phosphinic acid in benzene and heating the solution with ethylbenzeneoxychlorophosphine on the water bath in a reflux apparatus; it is exceedingly hygroscopic, and forms small, white crystals, which melt at 68°.

Di-ethylbenzenephosphonic acid, $(C_6H_4Et)_2PO{\cdot}OH$, is a bye-product in the preparation of ethylbenzenephosphinous acid, and is isolated in the form of the *copper* salt; the *silver* salt is amorphous.

Ethylbenzenephosphine, $C_6H_4Et{\cdot}PH_2$, is a transparent, highly-refractive liquid which boils at 200°; the *platinochloride* is a golden yellow, crystalline powder, and the *hydriodide* separates from water in lustrous, white crystals, melting at 118°.

Ethylbenzenediethylphosphine, $C_6H_4Et{\cdot}PEt_2$, is a colourless, highly-refractive liquid, having a penetrating odour; it boils at 268—270°, and has a sp. gr. = 0·929 at 17°. The *platinochloride* is reddish-white, and the *methiodide* crystallises in long, white needles, and melts at 135°; the *ethiodide* forms white needles, and when heated is resolved into its components without undergoing fusion.

Ethylbenzenephosphinophenylhydrazone, $C_6H_4Et{\cdot}P{:}N{\cdot}NHPh$, is obtained by the action of ethylbenzenechlorophosphine on phenylhydrazine dissolved in ether; it is a white crystalline powder, and melts at 139°.

[With FRITZ ROTHE and R. USTER].—*ψ-Cumylchlorophosphine*, $C_6H_2Me_3{\cdot}PCl_2$ [$Me_3{:}PCl_2$ = 1:2:4:5], obtained from ψ-cumene, phosphorus trichloride, and aluminium chloride, is a colourless, highly-refractive liquid, which boils at 280°, and has a sp. gr. = 1·2356 at 20°; it is also produced when the mercury derivative corresponding with symmetrical bromo-ψ-cumene (Abstr., 1895, i, 368) is heated with phosphorus trichloride in sealed tubes at 230—240°. *ψ-Cumyltetra-*

chlorophosphine, $C_6H_2Me_3\cdot PCl_4$, is a greenish-white crystalline mass, and melts at 75°. *ψ-Cumyloxychlorophosphine*, $C_6H_2Me_3\cdot POCl_2$, is crystalline and colourless; it melts at 63°, and boils at 307—308°.

ψ-Cumylphosphinous acid, $C_6H_2Me_3\cdot PHO\cdot OH$, is produced by the action of water on the chlorophosphine, and crystallises from alcohol in rhombic leaflets; it melts at 128°, and undergoes no change when exposed to the air. The *potassium*, *lead*, and *copper* salts are anhydrous, and the *barium* salt contains $3H_2O$; the *phenylhydrazine* salt crystallises in small white needles, and melts at 180°.

ψ-Cumylphosphonic acid, $C_6H_2Me_3\cdot PO(OH)_2$, is obtained by the action of water on the tetrachloro- and oxychloro-phosphines, and crystallises from water in white needles; it melts at 212°, and is sparingly soluble in cold water. The *hydrogen potassium*, *hydrogen barium*, and *silver* salts are anhydrous; the *hydrogen nickel* salt, with $4H_2O$, crystallises in lustrous, green leaflets. The *phenylic* salt melts at 62·5°, and boils above 360°; the *dianilide*, $C_6H_2Me_3\cdot PO(NHPh)_2$, crystallises from dilute acohol in lustrous needles, and melts at 197°. *Trianilido-ψ-cumylphosphonium chloride*, $C_6H_2Me_3\cdot(NHPh)_3Cl$, obtained by heating ψ-cumyltetrachlorophosphine with aniline hydrochloride at 170—180°, melts at 247°; the *bromide*, *iodide*, and *nitrate* melt at 259°, 220°, and 224—225° respectively, whilst the *hydroxide*, which is indifferent towards litmus, melts at 203·5°. The *phenylhydrazide* of ψ-cumylphosphinic acid, $C_6H_2Me_3\cdot PO(N_2H_2Ph)_2$, crystallises in small, lustrous needles, and melts at 208°; it reduces Fehling's solution when heated.

Chloro-ψ-cumylphosphonic acid [Me_3:P:Cl = 1:2:4:5:6] is produced when chlorine is passed into a solution of ψ-cumylphosphonic acid dissolved in glacial acetic acid, and crystallises in white, lustrous needles, melting at 235°; when treated with fuming nitric acid at low temperatures, it yields nitrochloro-ψ-cumylphosphonic acid, the hot acid converting it into dinitrochloro-ψ-cumene. The *hydrogen phenylhydrazine* salt crystallises from alcohol in small needles, and melts at 197·5°. 6:3-*Chloronitro-ψ-cumylphosphonic acid* crystallises from water in long, lustrous, pale yellow needles, and, when slowly heated, melts and decomposes at 227—228°. 3:6-*Dinitro-ψ-cumylphosphonic acid* forms small, white needles, and decomposes at 239° when slowly heated; if the temperature is raised rapidly, the nitro-acids explode. The *hydrogen phenylhydrazine* and *hydrogen aniline* salts of the dinitro-acid melt and decompose at 240° and 273° respectively, the *copper* salt crystallises in greenish needles containing $1H_2O$, and the *silver* and *hydrogen silver* salts crystallise from water.

Xylophosphonic acid, $COOH\cdot C_6H_2Me_2\cdot PO(OH)_2$ [= 1 : 2 : 4 : 5], obtained by oxidising ψ-cumylphosphonic acid in alkaline solution with potassium permanganate, melts at 258°, and, when heated above this temperature, yields metaphosphoric and xylenecarboxylic acids. The *silver* salt is sensitive to light. *Methylphthalophosphonic acid*,

$$(COOH)_2C_6H_2Me\cdot PO(OH)_2\ [? = 1:4:3:6],$$

is produced when the oxidation with permanganate is performed under modified conditions; it is a yellowish, hygroscopic powder, which melts at 185—190°; the *silver* salt is colourless.

Di-ψ-cumylphosphonic acid, $(C_6H_2Me_3)_2PO\cdot OH$, is obtained on treating with water the residue from the preparation of ψ-cumylchloro-

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phosphine after extraction with light petroleum. It forms highly refractive crystals, belonging to the monoclinic system, the axial ratios being $a:b:c = 0{\cdot}96:1:0{\cdot}983$; $\beta = 113°$. The acid melts at 202—203°, and is converted at 240—250° into ψ-cumene and *phosphino-ψ-cumene*, $C_9H_{11}PO_2$, a white, crystalline powder, which melts at 80°. The *potassium* salt of di-ψ-cumylphosphonic acid contains $1H_2O$, and the ammonium salt $2H_2O$; the *barium*, *lead*, *silver*, *cobalt*, *nickel*, and *copper* salts are anhydrous, but the two last-named contain $10H_2O$ when crystallised from aqueous ether.

Di-xylophosphonic acid, $(COOH{\cdot}C_6H_2Me_2)_2PO{\cdot}OH$, is produced on oxidising di ψ-cumylphosphonic acid with potassium permanganate; it melts at 185°, and the *silver* salt is not altered by exposure to light.

ψ-Cumylphosphine, $C_9H_{11}{\cdot}PH_2$, which is obtained when an alcoholic solution of ψ-cumylphosphinous acid is submitted to distillation in an atmosphere of carbonic anhydride, has a very disagreeable odour, and boils at 214—218°; it is rapidly oxidised on exposure to air, ψ-cumylphosphinous acid being produced. The *platinochloride* is yellow, and the *diethyl* derivative has a penetrating odour, boils at 274—275°, and yields a red, crystalline *platinochloride*; *methyldiethyl-ψ-cumylphosphonium iodide* crystallises from water in lustrous, rhombic plates, and melts at 160°.

Diphenoxy-ψ-cumylphosphine, $C_9H_{11}{\cdot}P(OPh)_2$, obtained by the action of ψ-cumylchlorophosphine on sodium phenoxide suspended in ether, is a viscous, colourless liquid, having a sp. gr. = 1·144 at 15°, and the refractive index = 1·5085; it boils at 283° under a pressure of 40 mm. Boiling water converts it into phenol and ψ-cumylphosphinous acid. *Diethoxy-ψ-cumylphosphine*, $C_9H_{11}{\cdot}P(OEt)_2$, is a colourless liquid, having the odour of the thiocarbimides; it has a sp. gr. = 1·048 at 15°, the refractive index = 1·505, and it boils at 232—233° under a pressure of 100 mm.

[With BERNHARD HECKER.]—*Mesitylchlorophosphine*, $C_6H_2Me_3{\cdot}PCl_2$, [$Me_3:PCl_2 = 1:3:5:4$], is prepared from mesitylene, phosphorus trichloride, and aluminium chloride, and crystallises in transparent plates a centimetre in length; it melts at 35—37°, forming a highly-refractive, colourless liquid, which boils at 273—275°, and has a sp. gr. = 1·205 at 15°. *Mesityltetrachlorophosphine*, $C_6H_2Me_3{\cdot}PCl_4$, melts at 70°. *Mesityloxychlorophosphine*, $C_6H_2Me_3{\cdot}POCl_2$, forms large, transparent crystals; it melts at 92—93°, and boils above 360°.

Mesitylphosphinous acid, $C_6H_2Me_3{\cdot}PHO{\cdot}OH$, crystallises from water in lustrous needles, and melts at 147°; the *potassium*, *ammonium*, *calcium*, and *copper* salts are crystalline and anhydrous. The *phenylhydrazine* salt melts and decomposes at 132°, and the *aniline* salt crystallises in long, yellowish needles; the *barium* salt contains $6H_2O$, and crystallises in long needles, which rapidly effloresce on exposure.

Mesitylphosphonic acid, $C_6H_2Me_3{\cdot}PO(OH)_2$, crystallises from dilute alcohol in long, colourless needles, and melts at 167°; the *hydrogen ammonium* and *silver* salts are anhydrous, whilst the *barium* salt contains $1H_2O$, and the *nickel* salt $8H_2O$. *Phosphinomesitylene*,

$$C_6H_2Me_3{\cdot}PO_2,$$

is produced when the phosphonic acid is heated with benzene and the oxychlorophosphine in a reflux apparatus at 40°; it separates

from chloroform in small crystals, and melts and decomposes at 215—216°.

β-Xylophosphonic acid, $COOH\cdot C_6H_2Me_2\cdot PO(OH)_2$, is obtained on oxidising mesitylphosphonic acid with potassium permanganate; it is amorphous, and melts at 245°, yielding metaphosphoric and mesitylenic acids at higher temperatures. The *silver* salt is decomposed by light. *Methylisophthalophosphonic acid*, $(COOH)_2C_6H_2Me\cdot PO(OH)_2$, is also formed during oxidation, and is very hygroscopic; it sinters at 215° and melts at 255°, yielding metaphosphoric and uvitic acids when heated above this temperature. The *silver* salt resists the action of light.

Mesitylphosphine, $C_6H_2Me_3\cdot PH_2$, is produced on submitting mesitylphosphinous acid to dry distillation in an atmosphere of carbonic anhydride; it forms colourless needles which melt at 40°, and under a pressure of 25 mm. it boils at 125°. The *platinochloride* forms orange crystals, and the *diethyl* derivative boils at 170°, and forms an orange *platinochloride*; *mesitylmethyldiethylphosphonium iodide* crystallises in colourless, lustrous needles, and melts, decomposing, at 125°. The *phenylhydrazone*, $C_9H_{11}P{:}N\cdot NHPh$, crystallises in small, lustrous needles, and melts at 135°.

[With OSWALD MEYER.]—*Cumylchlorophosphine*, $CHMe_2\cdot C_6H_4\cdot PCl_2$, is obtained from cumene, phosphorus trichloride, and aluminium chloride; it is a colourless liquid which boils at 268—270°, and has a sp. gr. = 1·190 at 12°. *Cumyltetrachlorophosphine*, $CHMe_2\cdot C_6H_4\cdot PCl_4$, is a white, crystalline mass which melts at 53—55°. *Cumyloxychlorophosphine*, $CHMe_2\cdot C_6H_4\cdot POCl_2$, melts at 35°, and boils at 183° under a pressure of 35 mm.

Cumylphosphinous acid, $CHMe_2\cdot C_6H_4\cdot PHO\cdot OH$, is a viscous oil, which dissolves sparingly in water; the *barium* salt contains $1H_2O$, the *phenylhydrazine* salt melts at 161°, and the *hydrogenphenylhydrazine* salt at 135°.

Cumylphosphonic acid, $CHMe_2\cdot C_6H_4\cdot PO(OH)_2$, produced on decomposing the tetrachloride with water, crystallises from cymene in lustrous prisms, melting at 139°; the *barium* and *silver* salts are anhydrous, and the *phenylhydrazine* salt crystallises in pale yellow leaflets, and melts at 172°.

Hydroxyisopropylphenylphosphonic acid, $OH\cdot CMe_2\cdot C_6H_4\cdot PO(OH)_2$, obtained by oxidising cumylphosphonic acid with potassium permanganate, separates as an oil from the aqueous solution; at 105—120°, the acid loses water, yielding *phenylallylphosphonic acid*,

$$C_3H_5\cdot C_6H_4\cdot PO(OH)_2,$$

a white powder which melts at 250°.

Dicumylphosphonic acid, $(CHMe_2\cdot C_6H_4)_2PO\cdot OH$, is a bye-product in the preparation of cumylphosphonic acid, and remains after removing the latter by means of light petroleum; it is a white powder, which becomes brown when heated, but does not melt. The *copper* and *aluminium* salts are anhydrous.

Cymylchlorophosphine, $C_6H_3MePr^{\alpha}\cdot PCl_2$, boils at 275—278°; the *tetrachlorophosphine* is a viscous liquid. *Cymylphosphinous acid* is liquid, and the *barium* salt contains $1H_2O$. *Cymylphosphonic acid* is also liquid, and the *hydrogen silver* and *silver* salts are decomposed by light; the *phenylhydrazine* salt crystallises from alcohol, and melts at 156°. *Cumyldiethylphosphine* boils at 260—270°. M. O. F.

Behaviour and Oxidation of Tetriodoterephthalic Acid and Tri-iododiamidobenzoic Acid. By JACOB LÜTJENS (*Ber.*, 1896, **29**, 2833—2839).—It is well-known that, whilst orthoiodobenzoic acid readily yields an iodoso-derivative on oxidation, the isomeric meta- and para-acids fail to do so. This difference in behaviour is possibly connected with the fact that, on occasion, the orthoiodoso-acid acts as a compound having a structure $C_6H_4<\begin{smallmatrix}I(OH)\\-CO-\end{smallmatrix}>O$, which the isomeric acids are unable to assume. On this supposition, diorthoiodobenzoic acid on oxidation should yield only a moniodoso-derivative,

$$C_6H_3I<\begin{smallmatrix}I(OH)\\-CO-\end{smallmatrix}>O,$$

and in like manner tetriodoterephthalic acid should yield a di-iodoso-acid.

2 : 4 : 6-*Tri-iodo*-3 : 5-*diamidobenzoic acid* is formed when a solution of dimetamidobenzoic acid in sulphuric acid is treated with one of iodine and iodic acid in caustic soda. It crystallises from hot, dilute alcohol in grey, felted needles. Attempts to eliminate its amido-groups were unsuccessful.

The author describes briefly the following salts of tetriodoterephthalic acid : The *calcium* salt, $C_6I_4(COO)_2Ca + 2H_2O$; the *strontium* salt, $C_6I_4(COO)_2Sr + 8H_2O$; the *barium* salt, $C_6I_4(COO)_2Ba + 4H_2O$; the *magnesium* salt, $C_6I_4(COO)_2Mg + 6H_2O$, and the *cadmium* salt,

$$C_6I_4(COO)_2Cd + 4H_2O,$$

are readily soluble in water; the *copper* salt, $C_6I_4(COO)_2Cu + 3H_2O$, forms blue-green crystals, and is sparingly soluble in water; the *methylic* salt, $C_6I_4(COOMe)_2$, crystallises in white needles, melting at 310—312°, the *ethylic* salt, $C_6I_4(COOEt)_2$, melts at 262·5°, and the *propylic* salt, $C_6I_4(COOPr)_2$, at 239°. The *chloride*, $C_6I_4(COCl)_2$, crystallises from chloroform, and melts at 279°; the properties of the latter are in accordance with those of other diortho-substituted benzoic acids, the substance being characterised by its excessive stability towards alkalis and hot water.

Di-iodosodi-iodoterephthalic acid, $C_6I_2(<\begin{smallmatrix}I(OH)\\-CO-\end{smallmatrix}>O)_2$, is produced when tetriodoterephthalic acid is warmed with a large excess of fuming nitric acid, and is most readily purified by means of its sodium salt. It is a a lemon-yellow powder insoluble in the ordinary media, and has very feeble acid properties, being precipitated from solutions of its salts by carbonic anhydride.

A. L.

Addition of Hydrogen Cyanide to Unsaturated Carboxylic Acids. By JULIUS BREDT and J. KALLEN (*Annalen*, 1896, **293**, 338—371).—*Ethylic cyanobenzylmalonate*, CN·CHPh·CH(COOEt)$_2$, is prepared by cautiously adding 33 per cent. hydrochloric acid to an alcoholic solution of ethylic benzylidenemalonate mixed with aqueous potassium cyanide, the liquid being well cooled during the operation; it crystallises in needles melting at 48·5°, and yields phenylcyanopropionic acid when hydrolysed with baryta.

Phenylcyanopropionic acid, CN·CHPh·CH$_2$·COOH, is obtained by heating alcoholic ethylic benzylidenemalonate with aqueous potassium cyanide on the water bath, and crystallises from dilute alcohol in

slender needles, melting at 150° ; the *ethylic* salt is produced when half the quantity of potassium cyanide and a much larger proportion of alcohol are employed, and forms a colourless liquid, which boils at 176° under a pressure of 16 mm. The *calcium* and *barium* salts crystallise in needles containing $3H_2O$, and the *silver* salt is a white, amorphous powder. When phenylcyanopropionic acid is hydrolysed with potash, phenylsuccinic acid is produced ; the anhydride melts at 150° (compare Spiegel, *Annalen*, 1883, **219**, 30).

Ethylic β-cyanobutyrate, $CN\cdot CHMe\cdot CH_2\cdot COOEt$, is obtained on heating ethylic ethylidenemalonate, dissolved in alcohol, with aqueous potassium cyanide for 7 hours at 60° ; it is a colourless, mobile liquid having a pleasant odour, and boils at 105—106°, under a pressure of 14 mm. Hydrolysis with baryta converts it into pyrotartaric acid.

Hydroalantolactonitrile, $CN\cdot C_{15}H_{21}O_2$, is produced when alantolactone (Abstr., 1895, i, 555) is dissolved in alcohol and heated with aqueous potassium cyanide for 12 hours in a reflux apparatus ; it crystallises in silvery scales, and melts at 132°.

Hydroalantolic acid nitrile, $CN\cdot C_{14}H_{21}(OH)\cdot COOH$, is obtained in the form of the *sodium* salt, when the lactone is treated with alcoholic sodium ethoxide ; the salt crystallises in stout needles, and yields the lactone when treated with acids. The *barium* and *calcium* salts are anhydrous, and the *silver* salt is amorphous. The *amine*, $NH_2\cdot CH_2\cdot C_{15}H_{21}O_2$, obtained on reducing hydroalantolactonitrile by adding sodium to the boiling solution in absolute alcohol, crystallises from dilute alcohol in aggregates of needles; it melts and decomposes at 171°, and the *platinochloride* is a bright yellow substance insoluble in ether and water.

Hydroalantolactonecarboxylic acid, $C_{15}H_{21}O_2\cdot COOH$, is formed when hydroalantolactonitrile is heated on the water bath with alcoholic potash so long as ammonia is liberated ; it crystallises from dilute alcohol in colourless, prismatic needles, melts at 137°, and boils at 250° under a pressure of 14 mm. The *sodium*, *barium*, and *calcium* salts are anhydrous, and the *silver* salt crystallises from boiling water.

Salts of hydroalantodicarboxylic acid, $OH\cdot C_{14}H_{21}(COOH)_2$, are obtained by hydrolysing the foregoing lactonic acid with alkalis, but on acidifying the solution, separation of the lactone takes place ; the *sodium* salt is very hygroscopic, and crystallises in small needles insoluble in alcohol. The *barium* and *calcium* salts dissolve with difficulty in water, and the *lead* salt is an amorphous powder insoluble in cold and hot water.

Orthohydroxyphenylsuccinic acid, $OH\cdot C_6H_4\cdot CH(COOH)\cdot CH_2\cdot COOH$, is produced on heating an alcoholic solution of coumarin with aqueous potassium cyanide for 6 hours in a reflux apparatus ; when rapidly heated, it melts at 150°, water being eliminated and the anhydride produced, this change taking place at 135° when that temperature is maintained for a considerable period. The aqueous solution develops a violet coloration with ferric chloride ; the *calcium* and *barium* salts are anhydrous. The *anhydride* melts at 134°, and boils at 200° under a pressure of 14 mm, a portion undergoing decomposition ; the *acetyl* derivative of the anhydride crystallises from a mixture of chloroform and ether, and melts at 90°.

M. O. F.

Condensation of Tannins with Formaldehyde. By C. EMANUEL MERCK (*Chem. Centr.*, 1896, i, 560; from *Ber. ü. d. Jahr.*, 1895, 14—19).—By treating plant extracts with formaldehyde in presence of hydrochloric acid, the tannins are easily withdrawn in the form of condensation products, which are named *tannoforms*. *Tannoform*, $CH_2(C_{14}H_9O_9)_2$, prepared by the condensation of tannin with formaldehyde, is a reddish-white powder which decomposes at 230°. It is soluble in alcohol and in dilute alkalis, with the latter forming a yellow or brownish-red solution, from which it is precipitated by acids. In warm, concentrated sulphuric acid, it dissolves, with production of a brown colour, and on further heating this turns green and then blue. With alcohol, either the green or the blue solution becomes first blue and then wine-red. *Quercitannoform*, $CH_2(C_{14}H_{13}O_7)_2 + H_2O$, prepared from oak bark tannin and formaldehyde, is a reddish-yellow powder, which blackens at 275°; it is insoluble in water, ammonia, and sodium hydroxide, and the brown colour of its solution in concentrated sulphuric acid is not affected by alcohol.

Quebrachitannoform, $CH_2(C_{26}H_{24}O_9)_2O$ or $CH_2(C_{26}H_{22}O_9)_2O$. *Rhatany tannoform*, $CH_2(C_{20}H_{16}O_7)O$, prepared from Rhatany tannin and formaldehyde with elimination of 4 molecules of water, is a yellowish-brown powder; its brownish-red solution in concentrated sulphuric acid rapidly turns red. *Myrobalans tannoform*, prepared from myrobalan tannin and formaldehyde, is a yellowish-brown powder with properties similar to those of tannoform, but its solution in concentrated sulphuric acid, on warming, becomes first green and then black. Like myrobalan tannin itself, it contains a little gallic acid and a considerable quantity of ellagic acid. This tannoform is an excellent protective against decubitus and hyperidrosis, and its effect is very different from that of tannin. E. W. W.

Oxidation of Diacetylcitraconfluoresceïn. By JOHN T. HEWITT and FRANK G. POPE (*Ber.*, 1896, **29**, 2824—2827).—The ethers of citraconfluoresceïn do not yield fluorone compounds when treated with alkaline potassium permanganate solution, owing to the readiness with which they suffer hydrolysis. Diacetylcitraconfluoresceïn, however, is oxidised by a hot solution of chromic acid in glacial acetic acid, yielding a *compound* difficult to purify, but which doubtless has the constitution $O\Big\langle\begin{matrix}C_6H_3(OAc)\\C_6H_3(OAc)\end{matrix}\Big\rangle C(OH)\cdot COOH$. It is readily soluble in sodium hydroxide, yielding a yellow solution; this darkens on heating, and, if an acid is then added, the *hydroxyfluoronecarboxylic acid*,

$$O\Big\langle\begin{matrix}C_6H_3(OH)\\C_6H_3O\end{matrix}\Big\rangle C\cdot COOH\ [C:OH:O = 1:3:6;\ C:O:O = 1:3:6],$$

is obtained in brown flocks. This acid, if moist, dissolves somewhat readily in acetone, and is deposited from it as a heavy, brown, crystalline powder; it is very sparingly soluble in dry organic solvents, but dissolves readily in alkalis, and shows no tendency to form a lactone, hence the hydroxyl-group is in the para-position relatively to the carbon atom of the pyrone nucleus. The *ammonium* salt of the acid yields characteristic red precipitates with various metallic salts, that produced by silver nitrate having the composition $C_{14}H_7O_5Ag$. A. L.

The Colour Base $(C_{15}H_{11}N)_x$ from Benzylphthalimidine. By SIEGMUND GABRIEL and ROBERT STELZNER (*Ber.*, 1896, **29**, 2743—2746. Compare Abstr., 1888, 143).—This substance, the molecular formula and constitution of which have not yet been ascertained, is converted by nitric acid into nitrobenzylidenephthalimidine (Abstr., 1885, 903, 1231). Chlorine converts the base into *β-dichloro-α-deoxybenzoïnorthocarboxylamide*, $CPhCl_2\cdot CO\cdot C_6H_4\cdot CO\cdot NH_2$, which can also be obtained by the action of chlorine on deoxybenzoïncarboxylamide. It crystallises in stellate groups of flat prisms, and melts, with evolution of gas, at 197°. The chloro-compound is reduced by hydriodic acid and phosphorus to benzylphthalimidine. When it is heated at 140° with acetic and hydrochloric acids, benzilorthocarboxylic acid is produced. When the chloro-compound is dissolved in normal alkali and the solution gently warmed, crystals of dihydrodiphthalyldiimide (Abstr., 1893, i, 372) are deposited. Concentrated potash (33 per cent.) converts it in the cold into a substance of the formula $C_{15}H_{11}NO_2$, which is also formed as a bye-product in the reduction of nitrobenzylidenephthalide (Abstr., 1888, 143). Finally, the chloro-compound is decomposed, with evolution of ammonia and formation of benzoic and phthalic acids when it is boiled with 10 per cent. potash. A. H.

Constitution of the Colour Bases of the Triphenylmethane Series. By HUGO WEIL (*Ber.*, 1896, **29**, 2677—2678).—A reply to von Georgievics (Abstr., 1896, i, 441, 690), upholding the author's previous statements (*ibid.*, 565). An interesting statement, made in support of the alleged stability of magenta in presence of alkalis, is that, from a solution of rosaniline carbonate (prepared by passing carbonic anhydride into a suspension of rosaniline in water), sodium chloride precipitates rosaniline hydrochloride, whilst the now colourless solution is alkaline from the presence of sodium carbonate.

C. F. B.

Hydroxy-derivatives of Tetramethyldiamidotriphenylmethane. By EMIL VOTOČEK (*Chem. Centr.*, 1896, i, 544; from *Listy Chem.*, 1895, 221—237).—The author obtained crystalline leuco-bases of dyes by the condensation of Michler's ketone with various phenols, namely, phenol, catechol, resorcinol, quinol, and pyrogallol. By oxidation of these bases, dichroic solutions of dyes are obtained, whilst the acetyl derivatives on oxidation yield green dyes which turn violet or blue on addition of alkalis. With para-amidophenol, no condensation could be effected. E. W. W.

History of Madder Dyestuffs. By CARL T. LIEBERMAN and SIEGFRIED FRIEDLÄNDER (*Ber.*, 1896, **29**, 2851—2854). — Runge (*Monogr. des Krapps und der Krappforbstoffe*, 1835) maintained that the madder dyes, obtained by Robiquet and Colin, &c., were impure substances, but regarded his own madder-red and madder-purple as chemical entities. The authors have examined samples of cloth coloured with Runge's dyes, and find that, whilst his madder red was pure purpurin, his madder-purple was impure, although rich in alizarin.

Samples of madder-dyeing from various localities were examined, and the results show that those from Avignon contained the largest proportion of alizarin, although contaminated with much purpurin.

The authors point out that the high proportion of alizarin in the French dyes accounts for the ease with which Robiquet and Colin achieved the isolation of pure alizarin. A. L.

Pinene. By J. C. W. FERDINAND TIEMANN and FRIEDRICH W. SEMMLER (*Ber.*, 1896, **29**, 3027—3034).—The authors now claim to have established the formula $CH\begin{cases} CH_2 \text{——} CH \\ \text{——} CH_2 \text{——} \\ CMe_2 \cdot CHMe \end{cases}C$ for the constitution of pinene, having traced the demolition of the hydrocarbon through the following phases.

1. Pinonic acid, $COOH \cdot CH_2 \cdot CH < \begin{matrix} CH_2 \cdot CO \\ | \\ CMe_2 \cdot CHMe. \end{matrix}$
2. Isoketocamphoric acid, $COOH \cdot CH_2 \cdot CH(CH_2 \cdot COOH) \cdot CMe_2 \cdot CMeO$.
3. Isocamphoronic acid, $COOH \cdot CH_2 \cdot CH(CH_2 \cdot COOH) \cdot CMe_2 \cdot COOH$.
4. Hydroxyisocamphoronic acid (salts),
   $COOH \cdot CH_2 \cdot CH[CH(OH) \cdot COOH] \cdot CMe_2 \cdot COOH$.
5. Isocamphoranic acid, $COOH \cdot CH_2 \cdot CH < \begin{matrix} CH(COOH) \\ CMe_2 \text{——} CO \end{matrix} > O$, or
   $\begin{matrix} COO \cdot CH \cdot COOH \\ | \quad\quad | \\ CH_2 \text{—} CH \cdot CMe_2 \cdot COOH. \end{matrix}$
6. Dimethyltricarballylic acid,
   $COOH \cdot CH(CH_2 \cdot COOH) \cdot CMe_2 \cdot COOH$, and
7. Hydroxytrimethylsuccinic acid, $COOH \cdot CMe(OH) \cdot CMe_2 \cdot COOH$.

The widely different conclusion regarding the structure of pinene to which von Baeyer has been led, is attributed to the employment by that investigator of more vigorous agents in breaking down the molecule, leading to pinonic acid, $C_{10}H_6O_3$, pinoylformic acid, $C_{10}H_{14}O_5$, pinic acid, $C_9H_{14}O_4$, and norpic acid, $C_8H_{12}O_4$. The existence of a picean ring (this vol., i, 83) in the two last-named substances is not regarded by the authors as evidence of the presence of this complex in pinonic acid, because the behaviour of pinonic and pinoylformic acids towards oxidising agents differs widely from that of pinic and norpic acids; moreover, the production of isoketocamphoronic acid,

$$COOH \cdot CH_2 \cdot CH(CH_2 \cdot COOH) \cdot CMe_2 \cdot CMeO,$$

from pinonic acid is difficult to reconcile with the formula

$$COOH \cdot CH_2 \cdot CH < \begin{matrix} CMe_2 \\ CH_2 \text{—} \end{matrix} > CH \cdot CMeO$$

for the latter substance. Von Baeyer regards isoketocamphoronic acid as having the constitution $COOH \cdot CH_2 \cdot CH(COOH) \cdot CMe_2 \cdot CH_2 \cdot CMeO$, representing isocamphoronic acid by the expression

$$COOH \cdot CH(CH_2 \cdot COOH) \cdot CMe_2 \cdot CH_2 \cdot COOH,$$

but this is scarcely consistent with the glutaric character of the substance, and with its conversion into terpenylic acid, which is analogous to the transformation of α-dimethylglutaric acid into γ-isocaprolactone.

The authors prefer to regard pinoylformic acid as having the constitution $COOH \cdot CH_2 \cdot CH < \begin{matrix} CH_2 \text{—} CO \\ | \\ CMe_2 \cdot CH \cdot COOH, \end{matrix}$ this being in agreement with the production of isoketocamphoronic acid when it is treated

with sodium hypochlorite. When dimethyltricarballylic acid, $COOH\cdot CH(CH_2\cdot COOH)\cdot CMe_2\cdot COOH$, is heated with bromine, the lactonic acid, $COOH\cdot CH<\begin{matrix}CH(COOH)\\CMe_2\text{---}CO\end{matrix}>O$, is formed, and this, when fused with caustic potash, yields oxalic and *as*-dimethylsuccinic acids.

M. O. F.

Condensation Products of Cyclic Ketones: Syntheses in the Terpene Series. By OTTO WALLACH (*Ber.*, 1896, **29**, 2955—2966. Compare Abstr., 1896, i, 572).—The synthetical pulegone, $C_{10}H_{16}O$, obtained by condensation of methylcyclohexenone with acetone (*loc. cit.*), is separated from bye-products by converting it into the *semicarbazone*, which forms two modifications, melting below 100° and at 144°, respectively; the ketone regenerated from these derivatives boils at 94—95° under a pressure of 14 mm., and under atmospheric pressure at 214—215°. The sp. gr. = 0·918, and the refractive index n_D = 1·46732, both at 20°. Representing natural or parapulegone by the formula $CMe_2:C<\begin{matrix}CH_2\cdot CH_2\\CO\text{---}CH_2\end{matrix}>CHMe$, the structure of the synthetical ketone will be either that of pseudopulegone,

$$COMe\cdot CH:C<\begin{matrix}CH_2\text{---}CH_2\\CH_2\cdot CHMe\end{matrix}>CH_2,$$

or of orthopulegone, $CMe_2:C<\begin{matrix}CO\text{——}CH_2\\CHMe\cdot CH_2\end{matrix}>CH_2$; the odour of the new ketone is scarcely distinguishable from that of the natural product, but in chemical properties they are widely different.

Pulegol, $C_{10}H_{17}\cdot OH$, is obtained by treating pulegone in ethereal or alcoholic solution with sodium; it is a viscous liquid, having the odour of terpineol, and boils at 103—104° under a pressure of 15 mm., and under atmospheric pressure at 215°. The sp. gr. = 0·912, and the refractive index, n_D = 1·4792 at 20°. When the warm alcohol is treated with phosphoric anhydride, the *terpene*, $C_{10}H_{16}$, is produced; this boils at 173—175°, and at 18° has the sp. gr. = 0·823, and the refractive index n_D = 1·4601. The *benzylidene* compound of synthetical pulegone is a yellowish, friable mass, and melts at 83—84°.

Synthetical pulegone is not the sole product of the action of acetone on methylcyclohexenone. A *compound*, $C_{13}H_{20}O$, is also formed, and the same substance is obtained when mesitylic oxide is employed; it boils at 179—183° in a vacuum.

[With DORRANCE]. — Benzylidenemethylhexenone (*loc. cit.*) condenses with acetone to form the benzylidene compound of synthetical pulegone.

Benzylhexahydrometatoluidine, $CH_2Ph\cdot C_6H_9Me\cdot NH_2$, is obtained by reducing the oxime of benzylidenemethylhexenone (m. p. 109—110°), in alcoholic solution, with sodium; it readily absorbs carbonic anhydride, and boils at 235—245°. The *hydrochloride* is solid, the *carbamide* crystallises in needles and melts at 185°, and the *acetyl* derivative at 168°.

Benzylmethylhexanol (*benzylhexahydrometacresol*),

$$CH_2Ph\cdot C_6H_9Me\cdot OH,$$

is formed when benzylidenemethylhexenone is reduced in alcoholic solution with sodium; it crystallises from methylic alcohol in beautiful,

colourless needles, and melts at 97°. Phosphoric anhydride converts it into *hexahydromethylfluorene*, $C_{14}H_{18}$, which boils at 128° under a pressure of 14 mm.; at 20° it has the sp. gr. = 0·99 and its refractive index n_D = 1·5455.

Biscyclopentenepentanone, $\begin{array}{l}CH_2\cdot CH_2\\ | \\ CH_2\cdot CH_2\end{array}\!>C:C<\!\begin{array}{l}CO-CH_2\\ \quad\quad\;\; | \\ CH_2\cdot CH_2\end{array}$, is obtained by treating pentanone with a concentrated solution of sodium ethoxide; it boils at 117—119° under a pressure of 12 mm., under atmospheric pressure at 253—254°. It has the sp. gr. = 1·0176, and the refractive index n_D = 1·52095, both at 20°; the *oxime* melts at 123—124°. The substance is capable of further condensation with benzaldehyde and pentanone under the influence of sodium ethoxide or hydrochloric acid.

Tricyclodipentenepentanone,

$$\begin{array}{l}CH_2\cdot CH_2\\ | \\ CH_2\cdot CH_2\end{array}\!>C:C<\!\begin{array}{l}CO-C=C-CH_2\\ \quad\quad\; | \quad\; | \\ CH_2\cdot CH_2\cdot CH_2\cdot CH_2\end{array}\!>CH_2$$

is a bye-product in the preparation of the foregoing compound, and is separated by means of the volatility of the latter in an atmosphere of steam; it crystallises from methylic alcohol in yellowish needles or leaflets, melts at 76—77°, and boils at 190° under a pressure of 12 mm. It does not yield an oxime.

[With OTTO M. RUETE].—*Biscyclomethylpentenemethylpentanone*,

$$\begin{array}{l}CH_2\cdot CHMe\\ | \\ CH_2-CO\end{array}\!>C:C<\!\begin{array}{l}CH_2\cdot CHMe\\ \quad\quad\quad | \\ CH_2\cdot CH_2\end{array},\text{ or }\begin{array}{l}CHMe\cdot CH_2\\ | \\ CH_2-CH_2\end{array}\!>C:C<\!\begin{array}{l}CH_2\cdot CHMe,\\ \quad\quad\quad | \\ CO-CH_2\end{array}$$

is a condensation product of methyl-3-pentanone-1. It is colourless and without odour, and boils at 127° under a pressure of 13 mm. The *oxime* melts at 94°, and the *alcohol*, obtained by reduction with sodium, boils at 121° under a pressure of 13 mm.

Biscyclohexenehexanone, $C_{12}H_{18}O$, is obtained from the cyclic hexenone and sodium ethoxide; it is volatile in steam, and forms yellow crystals. The *oxime* melts at 146—148°.

Biscyclomethylhexenemethylhexanone, $C_{14}H_{22}O$, is obtained from methylhexenone and sodium ethoxide, and also by withdrawing the elements of halogen hydride from the compounds $C_{14}H_{23}ClO$, and $C_{14}H_{23}BrO$, produced from methylhexenone and halogen hydride. It boils at 143—144° under a pressure of 10 mm.; its sp. gr. = 0·9635, and its refractive index n_D = 1·4955 at 20°. The oxime melts at 152°.

M. O. F.

French Oil of Roses. By JUSTIN DUPONT and JACQUES GUERLAIN (*Compt. rend.*, 1896, **123**, 700—702).—The authors have made a preliminary examination of two samples of French oil of roses distilled during the years 1895 and 1896. These samples differ considerably from the Bulgarian (Turkish) oil in their general characters, and possess a very much more fragrant smell. The following numbers are given.

	French, 1895.	French, 1896.	Bulgarian (average).
Sp. gr. 30°/15°	0·8225	0·8407	0·8650
Rotation at 30° (100 mm. tube)	− 6° 45′	− 8° 3′	− 3° 30′
Percentage of stearoptene	35	26	6 to 13

The stearoptene was separated completely from both of the above samples, and melted at 38° in the first case and at 33° in the second.

By a series of fractional crystallisations, two products were obtained from it, the one melting at about 39°, the other at about 24°; this confirms Bertram's statement that *two* solid hydrocarbons exist in rose oil, melting at 20° and 40° respectively, and is opposed to the observations of Markownikoff and Reformatsky (Abstr., 1893, i, 662; comp. also Abstr., 1894, i, 253). The two oils from which the stearoptene had been removed produced rotations of $-10° 30'$ and $-10° 42'$ respectively. The oils were heated for 1 hour with alcoholic potash, and the insoluble portion was separated and fractionated under a pressure of 20 mm. Four fractions were obtained, boiling at 110—120°, 120—125°, 125—150°, and 150—180°. From the first fraction, an optically inactive liquid was obtained boiling at 114—115° (20 mm.), having a sp. gr. = 0·8859, and possessing the odour of geraniol. It is therefore probably geraniol. From the alkaline liquid obtained in the hydrolysis of the oil, a syrupy acid having a powerful and characteristic smell was obtained by acidifying with sulphuric acid and extracting with ether. This will be studied. The above results point to the presence in the French oil of roses of a powerful lævo-rotatory ethereal salt which is hydrolysed on prolonged boiling with water. The hydrolysis of this salt in the preparation of the Turkish oil is thought by the author to account for the diminished fragrance of that oil as compared with the products they have examined, which were obtained by one distillation only.

A. C. C.

Camphor. By J. C. W. FERDINAND TIEMANN (*Ber.*, 1896, **29**, 3006—3026. Compare Abstr., 1895, i, 426, 675, 678).—*a*-Campholenonitrile, $CN{\cdot}CH_2{\cdot}CH{<}{\begin{matrix}CH_2-CH\\ \quad\ \Vert\\ CMe_2{\cdot}CMe\end{matrix}}$, is most conveniently prepared by heating camphoroxime (500 parts) with 25 per cent. sulphuric acid (1500—2000 parts) in a reflux apparatus for 15 minutes, the source of heat being removed as soon as action commences; it boils at 226—227°, and in a decimetre tube $a = +7·5°$. When hydrogen chloride is passed into an alcoholic solution of the nitrile, *a*-campholenic acid is produced, along with a certain quantity of isoamidocamphor.

a-Campholenamidoxime, $NOH{:}C(NH_2){\cdot}CH_2{\cdot}CH{<}{\begin{matrix}CH_2-CH\\ \quad\ \Vert\\ CMe_2{\cdot}CMe\end{matrix}}$, first obtained by Goldschmidt and Zürrer, is produced when *a*-campholenonitrile is heated with aqueous hydroxylamine during several days under pressure; it crystallises in white needles melting at 102°, and the hydrochloride melts at 181°.

a-Camphylamine, $NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH{<}{\begin{matrix}CH_2-CH\\ \quad\ \Vert\\ CMe_2{\cdot}CMe\end{matrix}}$, was obtained by Goldschmidt and Schulhoff on reducing alcoholic *a*-campholenonitrile with sodium; it boils at 111—112° under a pressure of 25 mm., and at 194—196° under atmospheric pressure. In a decimetre tube, $a = +6°$.

α-Campholenamide (Abstr., 1895, i, 676) crystallises in lustrous leaflets on adding petroleum to the solution in benzene; dissolved in alcohol, it has $[\alpha]_D = -4{\cdot}06°$. Although warm, dilute sulphuric acid converts the amide into the sulphate of isoamidocamphor, incautious treatment with the acid gives rise to dihydrocampholenolactone, with elimination of ammonia.

α-Campholenic acid, $COOH{\cdot}CH_2{\cdot}CH{<}\begin{array}{l}CH_2-CH\\ CMe_2{\cdot}\overset{\|}{C}Me\end{array}$, is obtained on hydrolysing the nitrile or the amide with alcoholic potash, and is identical with the product formed when β-dibromocamphor is heated with dilute alcohol and sodium amalgam. Prepared from this source, it has been known as hydroxycamphor, and its formation from β-dibromocamphor leads the author to regard the latter as having the constitution $CH\begin{array}{c}\diagup CHBr\cdot CO \diagdown\\ \text{——} CH_2 \text{——}\\ \diagdown CMe_2{\cdot}CMe \diagup\end{array}CBr$; when this is reduced, hydroxycamphor, $CH\begin{array}{c}\diagup CH_2\text{—}CO \diagdown\\ \text{——} CH_2 \text{——}\\ \diagdown CMe_2{\cdot}CMe \diagup\end{array}C{\cdot}OH$, is first formed, passing immediately into dihydrocampholenolactone or α-campholenic acid. α-Campholenic acid boils at 256°, and, in a decimetre tube, $\alpha = +9° 37'$, the *calcium* salt crystallises from alcohol in white needles; the ethylic salt boils at 222—224°, and, in a decimetre tube, $\alpha = +10° 20'$.

α-Dihydroxydihydrocampholenic acid,

$$COOH{\cdot}CH_2{\cdot}CH{<}\begin{array}{l}CH_2-CH{\cdot}OH\\ CMe_2{\cdot}\overset{|}{C}Me{\cdot}OH\end{array}$$

(compare Abstr., 1895, i, 676), was first obtained by Wallach on oxidising crude campholenic acid with potassium permanganate (Abstr., 1892, 1237); it is more conveniently prepared, however, by oxidising an ice-cold solution of sodium α-campholenate with 2 per cent. potassium permanganate, added to the liquid during 2 hours. The acid crystallises from water or chloroform, and melts at 144°; it has $[\alpha]_D = +58{\cdot}03°$.

l-*Pinonic acid*, $COOH{\cdot}CH_2{\cdot}CH{<}\begin{array}{l}CH_2-CO\\ CMe_2{\cdot}\overset{|}{C}HMe\end{array}$, is produced along with α-dihydroxydihydrocampholenic acid when α-campholenic acid is oxidised, and is also formed when α-dihydroxydihydrocampholenic acid is submitted to dry distillation, water being eliminated, a change which probably involves the formation of an intermediate product containing the ethylenic oxide group $\begin{array}{l}{=}C\text{—}\\ -\overset{|}{C}H\end{array}{>}O$, which undergoes atomic rearrangement into the residue, $\equiv CH{\cdot}CO$. *l*-Pinonic acid separates from water in tetragonal crystals, and melts at 98—99°, forming a colourless, viscous oil, which boils at 178—180° under a pressure of 12 mm.; it has $[\alpha]_D = -21{\cdot}4°$. The *oxime* forms white needles, and melts at 147°, and the *semicarbazone* crystallises from alcohol, and melts at 232°. The acid yields bromoform or carbon tetrabromide under the influence of alkali hypobromite, but the action proceeds with greater difficulty than in the case of inactive pinonic acid; con-

centrated sulphuric acid converts *l*-pinonic acid into methoethylheptanonolide, and the substance obtained from this source appears to be optically active. In all other properties, *l*-pinonic acid agrees with the inactive substance obtained from pinene.

Isoketocamphoric acid, $COMe\cdot CMe_2\cdot CH(CH_2\cdot COOH)_2$, is obtained alike from α-dihydroxydihydrocampholenic and *l*-pinonic acids by the oxidising action of chromic acid; it separates from ether in large, lustrous crystals, melts at 128—129° (Abstr., 1895, i, 478), and is optically inactive. The *oxime* crystallises in needles, and melts at 185—186°, and the *semicarbazone* at 187°.

Isocamphoronic acid, $COOH\cdot CMe_2\cdot CH(CH_2\cdot COOH)_2$, first obtained by Kachler on oxidising camphor with nitric acid, and subsequently by Kachler and Spitzer on oxidising the mixture of products obtained when β-dibromocamphor is reduced with sodium amalgam, is prepared from α-dihydroxydihydrocampholenic and *l*-pinonic acids by allowing chromic acid to act more vigorously on the substances than is permitted when isoketocamphoric acid is required; in order to separate the acid from terpenylic and terebic acids, it is precipitated with cupric acetate. Isocamphoronic acid melts at 166—167°; its ethylic salt boils at 195—200° under a pressure of 36 mm. According to the above expression, isocamphoronic acid contains a double glutaric acid grouping of the atoms, and, in consequence, yields an anhydride with great difficulty; prolonged treatment with boiling acetic chloride yields an anhydro-acid which dissolves readily in chloroform, and is so rapidly converted into isocamphoronic acid under the influence of water that it has not been found possible to purify it.

The constitution which von Baeyer ascribes to isocamphoronic acid (this vol., i, 82) is not in accordance with this observation; the conversion of the substance into terpenylic acid, which the author has shown to take place under the influence of concentrated sulphuric acid (this vol., i, 91, 158), agrees with the behaviour of α-dimethylglutaric acid when treated with the same agent, γ-isocaprolactone being formed. Moreover, the ready conversion of camphor into carvacrol, paracymene, and metacymene, and, further, the production of trimethylsuccinic acid or its anhydride (1) when camphoronic acid is submitted to dry distillation, (2) on oxidising camphoric acid with chromic acid (3) on heating trimethylpentanonedioic-acid,

$$COOH\cdot CHMe\cdot CMe_2\cdot CO\cdot COOH,$$

and (4) by the ultimate oxidation of camphoric acid with potassium permanganate, indicates the presence in the camphor molecule of one carbon atom to which two methyl groups are attached, and a second carbon atom combined with one methyl group; furthermore, these two carbon atoms are united directly with one another, becoming separated when carvacrol or cymene is produced from camphor.

M. O. F.

Crystallographic Properties of Substituted Camphors. By Jules Minguin (*Compt. rend.*, 1896, **122**, 1548—1550).—*Dextrogyrate benzylidenecamphor* forms rhombic prisms of 111° 45′ in which $b = 1000$ and $h = 801\cdot 6$. The faces observed are $m\ p\ g^3\ a^1\ b^{\frac{1}{2}}\ e^1\ e^2\ e^{\frac{1}{2}}$. The crystals being most commonly formed of $p\ m\ g^3\ b^{\frac{1}{2}}\ a^1\ e^1$. Sometimes e^1 and a^1 are abnormally developed and p and m disappear. No hemihedral faces are observed.

Lævogyrate benzylidenecamphor has precisely the same form and likewise shows no hemihedral faces.

Racemic benzylidenecamphor forms monoclinic prisms of 119° 10′, the inclination of the axes being 25°, whilst $b = 1000$ and $h = 996{\cdot}7$. The general form is $p\ m\ h^1\ b^1\ d^1$, the face p being highly developed.

Anisylidenecamphor forms rhombic prisms of 114° 15′, $b = 1000$ $h = 297{\cdot}4$. The faces observed are $m\ g^1\ g^3\ a^1\ e^1\ e^{\frac{1}{2}}\ b^{\frac{1}{2}}$, $b^{\frac{1}{2}}$ being excessively developed, whilst $a^1\ e^1\ e^{\frac{1}{2}}\ g^1$ are very small.

Methylsalicylidenecamphor.—The ortho-derivative of the preceding (para) compound forms monoclinic prisms of 93° 10′, the inclination being 23° 13′, and $b = 1000$, $h = 852{\cdot}9$. The general form is $p\ m\ g^1\ a^1\ h^1\ e^2$, the face g^1 being very small, whilst h^1 is always strongly developed.

Ethylsalicylidenecamphor forms monoclinic prisms of 103° 8′, the inclination being 26°, and for $b = 1000$, $h = 879{\cdot}6$. The common faces are $p\ m\ g^1\ h^1\ e^1\ b^{\frac{1}{2}}$, and of these $e^1\ g^1\ h^1$ are not always present.

The substitution of more or less complex radicles in the CH_2 group of camphor lowers the symmetry. Amongst those that crystallise in the rhombic system, the angles of the prisms do not greatly differ, and in the zone m there is always an angle of about 160° corresponding with a face g_3. The molecular grouping seems to remain the same, and the ratio of the linear dimensions of the primary form is the most variable element. Racemic benzylidenecamphor and the methyl- and ethyl-salicylidenecamphors differ but little in the zone ph, and the angles of inclination of the prisms are nearly the same.

Orthomethylsalicylidenecamphor has less symmetry than the para-isomeride. C. H. B.

Dammar Resin. By G. Glimmann (*Arch. Pharm.*, 1896, **234**, 584—589).—The resin was extracted in a large Soxhlet apparatus with absolute alcohol, and the alcoholic extract was poured into distilled water, whereon a pure white substance separated; a bitter principle remained dissolved in the water. The pure resin separated in this way melts at 100° and dissolves in ether, absolute alcohol, chloroform, benzene, carbon bisulphide, and sulphuric acid; when destructively distilled it yields a product containing phenolic compounds; the ethereal oil obtained by distilling the resin with steam boils at 82°, and smells of pepper.

Dammarolic acid, $OH{\cdot}C_{54}H_{77}O_3(COOH)_2$, is obtained by shaking the ethereal solution of the pure resin with a solution of potash (1 : 1000) and precipitating the acid by hydrochloric acid; it is freely soluble in alcohol, ether, chloroform, benzene, aniline, phenol, sulphuric acid, acetic acid, and carbon bisulphide; light petroleum dissolves it very sparingly. The *copper* and *potassium* salts were analysed, also an *acetyl* and a *benzoyl* derivative, which appear to warrant the above formula for the acid.

The ethereal solution from which the acid has been extracted contains *a-dammar-resen*, $C_{11}H_{17}O$, which melts at 65°, and dissolves in alcohol, ether, chloroform, sulphuric acid, and carbon bisulphide. The portion of the crude resin insoluble in absolute alcohol is only soluble in chloroform, and constitutes *β-dammar-resen.* It melts at 200°. The

following is the percentage composition of the dammar resin examined by the author.

Dammarolic acid	23·0
Water	2·5
Ash	3·5
Impurities	8·0
α-Dammar-resen	40·0
β-Dammar-resen	22·5
Loss (ethereal oil, bitter principle)	0·5

A. G. B.

Guaiacum Resin. By OSCAR G. DOEBNER and ED. LÜCKER (*Arch. Pharm.*, 1896, **234**, 590—610).—The following analysis was made by precipitating the alcoholic solution of the resin with alcoholic potash, which throws down potassium guaiaretate, evaporating the filtrate, dissolving the residue in water, precipitating the guaiaconic and guaiacic acids with hydrochloric acid, and separating them by means of ether, in which the former is soluble.

		Per cent.
Soluble in alcohol	Guaiaretic acid	11·15
	Guaiaconic acid	50·00
	Guaiacic acid (β-resin)	11·75
Insoluble in alcohol	Residue *	24·96
	Loss	2·14

* Containing :—

	Per cent.
Ash	2·10
Gum	9·64

Guaiaretic acid was prepared according to the recipe of Hlasiwetz (*Annalen*, 1859, **112**, 182; 1861, **119**, 206; 1864, **130**, 346). It forms white, lustrous laminæ and melts at 86°. Analyses of the acid are in accord with the formula $C_{20}H_{24}O_4$, not $C_{20}H_{26}O_4$; the *benzoyl* derivative, $C_{20}H_{23}O_4Bz$, forms nearly colourless crystals and melts at 131°. Dry distillation of the acid yields guaiacol, pyroguaiacin, and tiglic aldehyde.

Guaiaconic acid (Hadelich, *J. pr. Chem.*, 1862, **87**, 321) is a white, amorphous powder and melts at 74—76°. Analyses indicate the formula $C_{20}H_{24}O_5$, not $C_{19}H_{20}O_5$, for the acid, and since the acid is insoluble in alkali carbonates it cannot contain a free carboxyl group. The *dibenzoyl* derivative melts at 81—83°, and the *diacetyl* derivative at 61—63°. By destructively distilling the acid, tiglic aldehyde, guaiacol, and pyroguaiacin are obtained, and by fusing it with potash, protocatechuic acid, together with small quantities of volatile fatty acids and phenolic compounds.

Guaiacic acid (Hadelich's β-resin; *loc. cit.*) was not obtained in a pure condition; the *benzoyl* derivative, $C_{21}H_{19}Bz_3O_7$, is a white, crystalline powder and melts at 155—158°. By dry distillation of the acid, tiglic aldehyde and creosol were isolated.

"Guaiacum oil" (*guajaköl*) is prepared by boiling guaiacum resin with sodium carbonate solution, filtering from the resin, which separates on cooling, saturating the filtrate with carbonic anhydride, again filtering, and extracting with ether. The oil is left when the

ether is evaporated; it is somewhat freely soluble in water, and freely in alcohol and ether. By acidifying the alkaline solution after it has been extracted with ether, "*guaiacum yellow*," $C_{20}H_{20}O_7$, is precipitated, and may be crystallised in yellow octahedra, which melt at 115° and dissolve in strong sulphuric acid with a cornflower-blue colour. A. G. B.

Synthesis of the Acids of Guaiacum Resin. By OSCAR G. DOEBNER (*Arch. Pharm.*, 1896, **234**, 610—613).—Tiglic aldehyde (5 parts), guaiacol and creosol (9 parts, comprised of 1 mol. of each) were dissolved in glacial acetic acid, strong hydrochloric acid (2 parts) was added, and the mixture heated for 20 minutes on the water bath; the liquid was then poured into strong hydrochloric acid (250 c.c.), heated for 15 minutes, and finally poured into cold water. The brown resin which separated has the formula $C_{20}H_{24}O_4$, and is therefore isomeric with guaiaretic acid (see preceding abstract); from its formation, the constitution

$$CHMe{:}CMe{\cdot}CH[C_6H_2Me(OMe)(OH)]{\cdot}C_6H_3(OMe){\cdot}OH$$

may be ascribed to it. It is insoluble in water, soluble in alcohol, and dissolves in strong sulphuric acid with a cherry-red colour.

A similar resin, of the empirical formula of guaiaconic acid, was obtained by the condensation of tiglic aldehyde with a mixture of guaiacol (1 mol.) and pyrogallol dimethyl ether (1 mol.). It does not give a blue coloration with oxidising agents.

Finally, a resin, $C_{21}H_{26}O_6$, has been prepared from pyrogallol dimethyl ether (2 mols.) and tiglic aldehyde, which dissolves in strong sulphuric acid with a red colour.

The view that certain resins may be regarded as condensation products of aldehydes with phenols is upheld by these experiments. A. G. B.

Guaiacum Blue. By OSCAR G. DOEBNER (*Arch. Pharm.*, 1896, **234**, 614—620).—After enumerating the oxidising agents which are capable of producing guaiacum blue, the author points out that the colouring matter is an oxidation product of guaiaconic acid, and is best prepared by shaking 100 c.c. of a solution of this acid (10 grams) in 96 per cent. alcohol (1 litre) with a solution of ferric chloride (10 grams) in water (3 litres). The blue flocks which separate are rapidly filtered off, washed with cold water, and dried over calcium chloride in a vacuum protected from light. By subsequently washing with benzene, any unaltered guaiaconic acid may be removed. The blue powder thus prepared has the formula $C_{20}H_{20}O_6$ or $C_{20}H_{22}O_6$, the former being more in accord with its formation from guaiaconic acid than the latter is. It appears that the colour of the blue compound is dependent on the oxygen which it contains in excess of that in the parent guaiaconic acid, this oxygen being in much the same condition as that in which the second atom of oxygen exists in hydrogen peroxide; thus, a number of oxidising agents will bleach the colouring matter, themselves suffering reduction. The blue loses oxygen and is bleached at 100°. Its solutions in glacial acetic acid and in alcohol are deep blue, but they very rapidly lose oxygen, becoming colourless. This oxygen is probably not eliminated in the form of ozone, since,

when it is set free by a dilute acid, it does not liberate iodine from potassium iodide; this is also the case with the oxygen liberated from hydrogen peroxide by a dilute acid.

Regarding guaiaconic acid as consisting of a condensation product of tiglic aldehyde, guaiacol, and pyrogallol dimethyl ether, the author constructs a formula for the blue which is built on the lines of that for cœrulignone, the oxidation product of pyrogallol dimethyl ether.

In the well-known tests which depend on the formation of guaiacum blue, it is better to use guaiaconic acid itself than to use guaiacum.

A. G. B.

The Action of Formaldehyde on Aloïn. By C. EMANUEL MERCK (*Chem. Centr.*, 1896, i, 561; from *Ber. ü. d. Jahr.*, 1895, 21—23).—By the action of formaldehyde and concentrated sulphuric acid on aloïn, a condensation product, $CH_2{:}C_{17}H_{16}O_7$, is obtained as an amorphous, tasteless powder, which, on heating above 260°, becomes black. It dissolves in dilute sodium hydroxide solution, forming a yellow solution, from which it is reprecipitated by acids. It forms a yellow solution in concentrated sulphuric acid, and a reddish-yellow solution in concentrated nitric acid. E. W. W.

Bitter Principles contained in the Leaves of Leucodendron concinnum. By C. EMANUEL MERCK (*Chem. Centr.*, 1896, i, 561; from *Ber. ü. d. Jahr.*, 1895, 3—7).—From the leaves of this plant, which is native to the Cape and of the order of *Proteaceæ*, a glucoside *leucoglycodrin*, $C_{27}H_{42}O_{10}$ or $C_{27}H_{44}O_{10}$, may be obtained as a bitter, white powder, by evaporating the alcoholic extract and repeatedly dissolving the residue in alcohol and precipitating with ether. It has a specific rotatory power $[\alpha]_D = -40{\cdot}25°$ and is decomposed by water. By the action of 2 per cent. sulphuric acid at 100°, a brown oil is produced, which, when treated with acetic anhydride, yields white crystals and an almost colourless liquid. From this liquid, which reduces Fehling's solution, a phenylglucosazone melting at 181—192° can be obtained (δ-galactose or glucose?).

By further evaporation of the alcoholic extract, a second bitter principle, *leucodrin*, may be isolated, which is possibly identical with proteacin, obtained by Meiring Beck from the same plant. Leucodrin, $C_{15}H_{16}O_8$, has a specific rotatory power, $[\alpha]_D = -15{\cdot}45°$, and crystallises in white prisms which are very sparingly soluble in water, and only slightly so in cold alcohol. *Octacetylleucodrin*, $C_{15}H_8O_8Ac_8$, which melts at 188—190°, is formed by the action of acetic anhydride on leucodrin. (Compare Hesse, Abstr., 1896, i, 495). E. W. W.

A Crystalline Bitter Principle contained in Plumiera acutifolia. By C. EMANUEL MERCK (*Chem. Centr.*, 1896, i, 561; from *Ber. ü. d. Jahr.*, 1895, 11—13).—This substance, $C_{57}H_{72}O_{33} + 2H_2O$, obtained by evaporation of the alcoholic extract, melts at 157—158° and forms a colourless solution in concentrated sulphuric acid, which, on warming, turns yellow, reddish-yellow, brownish-red, or black. Its solution in concentrated nitric acid is also colourless, but becomes yellow on warming, and, similarly, the solution in sodium hydroxide turns yellow on boiling. This substance cannot be identical with plumieride, which has beeen isolated by Boorsma. E. W. W.

Compounds contained in Radix imperatoriae ostruthium. By C. EMANUEL MERCK (*Chem. Centr.*, 1896, i, 561; from *Ber. ü. d. Jahr.*, 1895, 8—10).—In the taproot of this plant three substances have already been found, namely, peucedanin, oxypeucedanin, which the author regards as a homogeneous compound in opposition to the views of Hlasiwetz and Weidel, and ostruthin. The author has obtained a new substance *osthin* $C_{15}H_{16}O_5$ which crystallises from dilute alcohol in slender, yellow needles, melts at 199—200°, and is insoluble in water. In concentrated sulphuric acid, it forms a yellow solution, which, on warming, becomes dark red. Its solutions in alkalis and ammonia are also yellow. *Diacetylosthin*, $C_{15}H_{14}O_5Ac_2$ melts at 183—186°. *Monoacetylosthin* melts at about 171—180°. In the original paper, a table of the melting points, solubilities, &c., of these four plant substances is given. E. W. W.

Synthesis of Pyridine Compounds from Ethereal Salts of Ketonic Acids and Ethylic Cyanacetate in Presence of Ammonia or Amines. By ICILIO GUARESCHI (*Chem. Centr.*, 1896, i, 601—603; from *Estr. Mem. Reale Accad. Sci. Torino*, ii, 46).—By the action of ammonia on homologues of ethylic acetoacetate, an ethereal salt of an amido-acid, $NH_2 \cdot CMe{:}CMe \cdot COOEt$, and an amide of a β-ketonic acid, $COMe \cdot CHMe \cdot CO \cdot NH_2$, are formed. But in the presence of ammonia, or an amine, the cyanacetamide first produced reacts with the β-ketonic acid amide to form a pyridine derivative, the condensation taking place with ease at the ordinary temperature. In this way, ethylacetoacetamide and ethylic cyanacetate form an ammonium salt, $NH_4 \cdot N{<}{\substack{CO \cdot CHEt \\ CO \cdot C(CN)}}{>}CMe$, from which hydrochloric acid liberates an acid compound of a similar constitution, or more probably possessing a composition represented by the formula,

$$N{<}{\substack{C(OH) \cdot CHEt \\ CO\text{——}C(CN)}}{>}CMe \quad (I).$$

The author has found that the reactions take place directly between cyanacetamide and β-ketonic acid amides or ethereal salts of ketonic acids, and similarly also between ketonic acid amides and ethylic cyanacetate. The new compounds thus formed have acid properties, yield dyes and, with ferric chloride, give a bluish-violet coloration or precipitate. Those derived from ethylic acetoacetate, and containing the group $-CH_2 \cdot C(OH){\equiv}$, form precipitates with copper sulphate and acetate, and become coloured by the action of potassium nitrite or of bromine water, whilst those containing the substituted group,

$$-CHMe \cdot C(OH){\equiv},$$

do not give these reactions.

To all these new substances, the author gives formulæ analogous to (I), representing them as $\alpha\beta'$-dihydropyridine derivatives, and regarding them also as derived from glutaconimide,

$$NH{<}{\substack{CO \cdot CH_2 \\ CO \cdot CH}}{>}CH.$$

When an amine is employed instead of ammonia, the resulting compounds contain an alkyl group directly united to nitrogen, and as these also have acid properties, this acidity cannot be ascribed to the presence

of an imide group, but the presence of a hydroxyl group must be assumed as in the formula, $NMe<\substack{C(OH):CH \\ CO\cdot C(CN)}>CMe$ (II). Similarly, the compound obtained from methylamine and ethylic methylaceto-acetate is to be regarded as containing a hydroxyl group, since it forms a silver compound, and with ferric chloride gives a coloration, although this is very fugitive. Its formula is therefore written,

$$NMe<\substack{C(OH):CMe \\ CO-C(CN)}>CMe, \text{ (III)}.$$

The constitution of the compounds which do not contain substituted imide groups the author prefers, for the present, to write in accordance with the formula (II) rather than with the formula

$$NH<\substack{C(OH):CH \\ CO\cdot C(CN)}>CMe.$$

3-*Cyano*-6-*hydroxy*-4-*methyl*-5-*ethyl*-$\Delta^{3,6}$-*dihydropyridone* (Formula (I)), prepared from ethylacetoacetamide, ammonia, and ethylic cyanacetate, melts at 234—235°, and is slightly soluble in cold water. The ammonium and the copper salts, $(C_9H_9N_2O_2)_2Cu$ and $C_9H_8CuN_2O_2$, have been analysed, and the sodium and magnesium salts prepared.

3-*Cyano*-6-*hydroxy*-4-*methyl*-$\Delta^{3,6}$-*dihydropyridone* or *cyanomethylglutaconimide*, $N\lessgtr\substack{C(OH)\cdot CH_2 \\ CO-C(CN)}>CMe$, is obtained by the action of ethylic acetoacetate, ammonia, and ethylic cyanacetate; at 295°, it becomes brown, and is charred at 300—304°; it yields a bromine derivative, which is decomposed by water or alcohol. By means of this reaction, the author proved that acetoacetamide is formed by the action of ammonia on ethylic acetoacetate. The ammonium, sodium, barium, silver, copper, and copper ammonium salts were analysed. The author was unable to determine whether the cyanodihydropyridinecarboxylic acid prepared by Held from ammonia and ethylic cyanacetate is identical with this compound.

3-*Cyano*-6-*hydroxy*-1-*methyl*-$\Delta^{3,5}$-*dihydropyridone* or *cyanomethylglutaconmethylimide* (Formula (II)), prepared from ethylic acetoacetate, methylamine, and ethylic cyanacetate, melts at about 285°, and its silver salt was analysed. The 1-*ethyl* compound or *cyanomethylglutaconethylimide*, which melts at about 242°, and the 1-allyl compound or *cyanomethylglutaconallylimide*, which melts at 222°, may be obtained by similar reactions.

3-*Cyano*-6-*hydroxy*-4-*methyl*-5-*ethyl*-$\Delta^{3,6}$-1-*dihydropyridone*, or *methylcyanomethylglutaconimide*, prepared from methylacetoacetamide, ammonia, and ethylic cyanacetate, melts at 270—272°. The ammonium, sodium, silver, barium, and copper salts were analysed. 3-*Cyano*-6-*hydroxy*-1 : 4 : 5-*trimethyl*-$\Delta^{3,5}$-*dihydropyridone* (Formula (III)), prepared from ethylic methylacetoacetate, methylamine, and ethylic cyanacetate, melts at 264—265°. With ferric chloride, it first gives a coloration, and is then oxidised to a compound which melts at 235°. *Amidobenzoylacetamide*, $NH_2\cdot CPh:CH\cdot CO\cdot NH_2$, which melts at 164—165°, and *cyanophenylglutaconimide*, which melts at 280—282°, are obtained by the interaction of ethylic benzoylacetate, ammonia, and ethylic cyanacetate.

E. W. W.

Stereochemistry in the Piperidine Series. By CARL D. HARRIES (*Ber.*, 1896, **29**, 2730—2731).—It has been already stated that vinyldiacetonamidoxime, on reduction with zinc and alcoholic hydrochloric acid, yields paramidotrimethylpiperidine. Further investigation showed that this oxime, on treatment with sodium and boiling amylic alcohol. was reduced to an isomeric paramidotrimethylpiperidine, the two amines being easily identified by means of their hydrochlorides, that of the former being generally oily, whilst that of the latter is a fine, crystalline solid. On treating the two bases with nitric acid, two hydroxyalkylamines (hydroxytrimethylpiperidines) are produced, the first being the compound (m. p. 123°) obtained by E. Fisher from vinyldiacetonamine by direct reduction, the second a compound melting at 160—161°. Both these compounds are also produced by the reduction of vinyldiacetonamine (oxytrimethyltetrahydropyridine) with sodium amalgam, and can be separated by fractional crystallisation. The former (m. p. 123°) is, however, not a homogeneous substance, but is a mixture of the base melting at 160—161°, with a new hydroxytrimethylpiperidine melting at 137—138°, the two being easily separated by means of their hydrochlorides. Both the compound melting at 160—161°, and the mixture (m. p. 123°) pass, on treatment with sodium amyloxide, into the stable compound melting at 137—138°. This subject will be treated more fully in a paper to be published in the *Annalen*. J. F. T.

Diphenylindone. By ADOLF DAHL (*Ber.*, 1896, **29**, 2839—2842. Compare Abstr., 1896, i, 146).—When diphenylindone is heated with hydriodic acid and phosphorus during 6 hours at 150—160°, *triphenylpropane*, $CHPh_2\cdot CHMePh$, is produced. It distils unaltered at 365°, solidifying to a hard, white mass; no crystalline derivative could be obtained.

Triphenyllactic acid is formed when diphenylindone is fused with potash at a moderate temperature. It crystallises from glacial acetic acid in yellowish crystals resembling those of common salt, and melts at 189°. Its constitution has not yet been definitely ascertained.

Methylic triphenylacrylate occurs in the bye-products obtained in the preparation of diphenylindone (*loc. cit.*). It crystallises from light petroleum in yellow needles, melting at 136°, and yields triphenylacrylic acid on hydrolysis. A. L.

Quinolineoxyquinolines. By PAUL COHN (*Monatsh.*, 1896, **17**, 667—671).—When 2′-chloroquinoline is heated with excess of 1-hydroxyquinoline, a reaction takes place, the evolution of hydrogen chloride being violent at 165°. The product, $C_9NH_6\cdot O\cdot C_9NH_6$, crystallises in yellow needles, and melts at 175° (uncorr.). The yellowish *hydrochloride*, $C_{18}H_{12}N_2O,HCl$, which is decomposed by water, the yellow *platinochloride*, $C_{18}H_{12}N_2O,H_2PtCl_6$, and the brownish-yellow *palladiochloride*, $C_{18}H_{12}N_2O,H_2PdCl_4 + H_2O$, were also prepared.

2′-Chloroquinoline also reacts with 3-hydroxyquinoline, but less readily. The product, isomeric with that described above, crystallises in yellowish needles, and melts at 120°; the yellow *platinochloride*, $C_{18}H_{12}N_2O,H_2PtCl_6$, was also prepared and analysed. C. F. B.

The Isorosindulines. By OTTO FISCHER and EDUARD HEPP (*Ber.*, 1896, **29**, 2752—2760).—The authors propose to retain the name isorosinduline in the sense in which they have previously (*Annalen*, **272**, 306) employed it, and to apply the term pseudorosinduline to the compounds called isorosindulines by Kehrmann (*Annalen*, **290**, 247). They have examined the isorosinduline prepared by Nietzki and Otto (Abstr., 1888, 843) from quinonedichlorodiimide and phenyl-β-naphthylamine, in order to ascertain in what respects it is analogous to the safranines.

Phenylisorosinduline, $NPh:C_6H_3<\genfrac{}{}{0pt}{}{N-}{NPh}>C_{10}H_6$, is prepared by the action of nitrosodiphenylamine on β-naphthylphenylamine. The *hydrochloride* crystallises in long, flat prisms with a copper-red lustre. The *nitrate* crystallises well in thick prisms, which have a metallic lustre. The base also forms crystals, which have a coppery lustre. It melts at 169—171°, and imparts a blue colour to sulphuric acid. Concentrated hydrochloric acid at 230—240° converts the base into *isorosindone*, $O:C_6H_3<\genfrac{}{}{0pt}{}{N-}{NPh}>C_{10}H_6$. This substance is best prepared from nitrosophenol and β-naphthylphenylamine, and is a weak base, the *hydrochloride* of which dissociates in aqueous solution. The free base crystallises in prisms, which have a dark bronze lustre, and melt at 223—224°. With ferric chloride, the hydrochloride forms a characteristic *double salt*, crystallising in golden yellow needles.

Hydroxyisorosindone, $O:C_6H_7(OH)<\genfrac{}{}{0pt}{}{N-}{NPh}>C_{10}H_6$, is formed when isorosindone is boiled with concentrated alcoholic potash; it crystallises in red needles, which have a bronze lustre. The *potassium salt* is readily soluble in water, sparingly in potash.

Methoxyisorosindone crystallises in needles, which melt at 274°, and have a greenish lustre.

Anilidoisorosinduline, $NH:C_6H_2(NHPh)<\genfrac{}{}{0pt}{}{N-}{NPh}>C_{10}H_6$, is obtained by the action of aniline and its hydrochloride on isorosinduline in alcoholic solution. The *hydrochloride* crystallises in prisms, with a greenish lustre. The free base forms brownish-red needles, which have a bluish lustre and melt at 151—152°. *Phenylanilidoisorosinduline* is formed when isorosinduline is heated at 150—160° with aniline and aniline hydrochloride, and crystallises with 1 molecule of benzene in needles which have a dark bronze lustre. *Anilidoisorosindone* is formed when anilidoisorosinduline is heated with hydrochloric acid at 160—170°; it crystallises in lustrous needles, with a bronze lustre.

Ethylisorosinduline, $NH:C_6H_3<\genfrac{}{}{0pt}{}{N-}{NEt}>C_{10}H_6$, is obtained by the reaction of quinonedichlorodiimide and β-naphthylethylamine. The *hydrochloride* forms short, flat, red prisms; the *nitrate* is less soluble than the hydrochloride, and crystallises in dark needles, which have a bronze lustre.

Ethylisorosindone forms slender, brownish-red needles, and melts at 178°; the *hydrochloride* crystallises in dark brown prisms.

Isorosinduline is converted by the action of nitrous acid into a diazo-compound. When this solution is treated with alcohol, nitrogen is evolved, and phenylnaphthophenazonium chloride is produced identical with the substance formed when rosinduline itself is treated in a similar manner. When the diazo-solution is treated with alcohol, and then, after a time, with a large excess of ammonia, rosinduline is formed, so that by this reaction the isorosinduline can be converted into rosinduline. A. H.

Azonium Compounds from Aposafranine, Rosinduline, and their Isomerides. By FRIEDRICH KEHRMANN and W. SCHAPOSCHNIKOFF (*Ber.*, 1896, **29**, 2967—2972. Compare this vol., i, 107.)—In consequence of Fischer and Hepp's publication (preceding abstract), the authors describe the following compounds which they have prepared.

An additive compound of phenylphenazonium chloride and ferric chloride, $C_{18}H_{13}N_2Cl,FeCl_3$, was prepared by the method previously described. If prepared from pure aposafranine, it crystallises readily from its acetic acid solution, otherwise a black, tarry mass is obtained; the crystals are light reddish-brown, thick needles, and melt at 186°. It is readily soluble in water, and in boiling alcohol and acetic acid, but practically insoluble in a saturated ferric chloride solution, in 20 per cent. hydrochloric acid, and in ether.

Phenylphenazonium nitrate, $C_{18}H_{13}N_2 \cdot NO_3$, was prepared from a cold, aqueous solution of the ferric chloride compound; this was rendered slightly alkaline by adding cold, dilute ammonium carbonate solution drop by drop, filtered into a few drops of dilute nitric acid, and then saturated with pure sodium nitrate. After the lapse of several days, the nitrate separated in reddish-brown crystals. It crystallises from alcohol in thick cubes, melts at 192°, and is readily soluble in water and alcohol.

Phenylnaphthophenazonium chloride forms an additive compound with ferric chloride, which can be obtained by deamidating either rosinduline or Nietzki and Otto's isorosinduline, and has already been described.

Phenylnaphthophenazonium nitrate, $C_{22}H_{15}N_2 \cdot NO_3$, recrystallised from alcohol, forms orange-yellow plates, melts at 225°, and is moderately soluble in cold water.

Phenylnaphthophenazonium platinochloride $(C_{22}H_{15}N_2)_2PtCl_6$, is a brick-red, crystalline powder, practically insoluble in water.

Phenylnaphthophenazonium dichromate, $(C_{22}H_{15}N_2)_2Cr_2O_7$, is also a red, crystalline powder which is insoluble in water. The *iodide*, $C_{22}H_{15}N_2I$, crystallises from alcohol in black plates. J. J. S.

Some Phenyltriazoles. By ASTRID CLEVE (*Ber.*, 1896, **29**, 2671—2677).—This paper has been published earlier than was originally intended on account of the work done on the same subject by Young (Trans., 1895, 1063). The oxytriazoles that Widman has prepared (Abstr., 1896, i, 629) by treating α-acidylphenylsemicarbazides with dilute alkaline hydroxides, were converted into chlorotriazoles by heating them for 3—5 hours at 150° in a sealed tube with the calculated quantity of phosphoric chloride, together with a little

phosphorus oxychloride. The chlorotriazoles were then reduced to triazoles by heating them for about 3 hours at 150—160° in a sealed tube with excess of concentrated hydriodic acid (sp. gr. 1·7)and a little red phosphorus. The triazoles are weak bases; the chlorotriazoles, on the other hand, seldom form hydrochlorides.

3-*Chloro*-1:5-*diphenyl*-1:2:4-*triazole*, $NPh<\begin{matrix} N = CCl \\ | \\ CPh:N \end{matrix}$, melts at 96°; the reddish-yellow *platinochloride* decomposes at 195°. 1:5-Diphenyltriazole melts at 91°, its yellowish-white *picrate* at 139°; the platinochloride crystallises with $4H_2O$ (and also with $3H_2O + 2HCl$?). 3:1:5-*Methoxydiphenyltriazole* was prepared by treating the hydroxytriazole in alcoholic solution with sodium methoxide and methylic iodide; it melts at 88°, and has basic properties. 3-*Chloro*-1-*phenyl*-5-*isopropyltriazole* melts at 56°, the *triazole* itself at 58°. 3-*Chloro*-1-*phenyl*-5-*propyltriazole* and the corresponding *triazole* were obtained as oils; the yellowish-white *picrate* of the latter melts at 128—130°, and the *platinochloride* crystallises with $4H_2O$. 3-*Chloro*-5-*butylphenyltriazole* and the corresponding triazole are also oils.

C. F. B.

Asymmetric Nitrogen (IV.) Isoconiine. By ALBERT LADENBURG (*Ber.*, 1896, **29**, 2706—2709).—The existence of isconiine having been called in question, the author now brings forward a series of experiments, showing that it is in reality a homogeneous substance, and not a mixture of *d*- and *r*-coniine.

The platinochloride of the compounds, produced by the distillation of *d*-coniine hydrochloride with zinc dust, behaves differently from the platinochloride of a mixture of *d*- and *r*-coniine; in the former case, a crystalline residue remains after treatment with a mixture of alcohol and ether, whilst in the latter the platinochloride entirely dissolves. This insoluble residue, which is the platinochloride of isoconiine, must therefore be free from *d*- and *r*-coniine.

Similarly, the rotation of benzoylisoconiine is very different from that of the benzoyl compound of a mixture of *d*- and *r*-coniine.

Finally, no pure *d*-coniine (rotatory power 18·3°) could be isolated from isoconiine, which would be the case were it a mixture of *d*- and *r*-coniine.

J. F. T.

Tropinic Acid. By GIACOMO L. CIAMICIAN and PAUL G. SILBER (*Ber.*, 1896, **29**, 2975—2976. Compare Abstr., 1896, i, 513).—The authors state that the aurochloride of the base, previously described by them as obtained by the action of hydriodic acid and phosphorus on tropinic acid, has proved not to be identical with α-methylpyrolidine aurochloride, as was at first thought possible. The base is probably a trialkylamine, obtained by the complete decomposition of the tropinic acid molecule.

J. J. S.

Attempts to Determine the Constitution of Tropanine and Granatanine Bases by Cryoscopic Methods. By FELICE GARELLI (*Ber.*, 1896, **29**, 2972—2975. Compare Abstr., 1894, i, 157; 1895, ii, 205).—The author has previously shown that similarly-constituted

substances can form solutions, which, on cooling, yield abnormal results for the depression of the freezing point. This phenomenon can be made use of in solving questions as to the constitution of different compounds. As regards tropanine and granatanine, the author is able to show that their cryoscopic behaviour agrees with the constitutions already deduced from chemical considerations. Both are to be regarded as containing two nuclei, like naphthalene, the two rings, however, being joined respectively in the para- and meta-positions in the two compounds.

Normal freezing point depressions were obtained with the two compounds in benzene and also in diphenyl solutions, but abnormal results in naphthalene solutions. Special precautions were taken on account of the readiness with which the bases combine with water and carbonic anhydride. J. J. S.

Alkaloids contained in the Seeds of Blue and White Lupines. By SHERMANN DAVIS (*Chem. Centr.*, 1896, i, 708—709; from *Apoth. Zeit.*, 11, 94—95).—A comparison of the alkaloids obtained from the seeds of *Lupinus angustifolius* and *L. albus*, respectively, led to the following conclusions. The composition of these compounds or *lupanines* is represented by the formula, $C_{15}H_{24}N_2O$, ascribed to them by Siebert (Abstr., 1892, 223), and by Soldaini (Abstr., 1896, i, 193). The lupanine from *L. albus* described by Soldaini as deliquescent is identical with the liquid lupanine from the same plant, and also with the liquid alkaloid obtained by Siebert from *L. angustifolius*. The identity of these compounds was proved by comparison of numerous salts, both chemically and crystallographically. This alkaloid, which the author names *dextrolupanine*, can in reality be readily obtained in a crystalline form, separating from light petroleum in colourless needles, which melt at 44°, and whose aqueous solution is dextrorotatory.

Soldaini's solid lupanine from *L. albus*, which melts at 99° and is optically inactive, has a composition represented by the formula $C_{15}H_{24}N_2O$, or $C_{30}H_{48}N_4O_2$. By converting it into thiocyanate, it may be separated into two components, dextro- and lævo-lupanine respectively. The free bases obtained from these salts form colourless needles which melt at 44°, and re-form the original inactive lupanine when mixed in equal parts. The dextro-component is identical with the dextro-lupanine obtained from blue and white lupines. None of the groups OH, OMe, CO, or COH, is present in lupanines. By the action of bromine on dextrolupanine hydrochloride in alcoholic solution, two new bases, $C_8H_{15}NO$ and $C_7H_{11}NO$, are obtained, each of which contains a hydroxyl group. The constitution of lupanine is, therefore, probably represented by the formula $C_8H_{15}N{\cdot}O{\cdot}C_7H_{11}N$.

E. W. W.

The Alkaloids of Corydalis. (By ERNST A. SCHMIDT (*Arch. Pharm.*, 1896, **234**, 489—491. Compare the following abstract).—Corydaline and corybulbine behave towards iodine in a similar manner to canadine (Abstr., 1894, i, 479). The details of the experiments are given in the following abstract. A. H.

The Alkaloids of Corydalis Cava. By H. ZIEGENBEIN (*Arch. Pharm.*, 1896, **234**, 482—537. Compare the preceding abstract).—The alkaloids were obtained from *Corydalis cava* by the method described by Freund and Josephi (Abstr., 1894, i, 100). The author finds that the formula of corydaline is most probably $C_{22}H_{27}NO_4$, in agreement with Freund and Josephi, whereas Dobbie and Lauder (Trans., 1892, 605) have proposed the formula $C_{22}H_{29}NO_4$. The hydrochloride could not be obtained crystalline. The hydrobromide and hydriodide are white when pure, but become yellow when exposed to the air. The *nitrate* crystallises in lustrous tablets melting at 198°. The *aurochloride*, $(C_{22}H_{27}NO_4,HCl)_2,AuCl_3$, crystallises in very characteristic rosettes of needles melting at 207°. A compound of the normal formula could not be obtained. Hemipinic acid was obtained by the oxidation of the alkaloid, the result previously published by Dobbie and Lauder (Trans., 1894, 57) being thus confirmed.

When corydaline is treated with iodine and alcohol, it is converted into *dehydrocorydaline hydriodide*, $C_{22}H_{23}NO_4,HI$, 4 atoms of hydrogen being removed from the molecule. This substance crystallises with $2H_2O$ and forms lustrous, pale yellow needles. The corresponding *hydrochloride*, $C_{22}H_{23}NO_4,HCl + 4H_2O$, crystallises in yellow plates and prisms. The *aurochloride* has the normal formula and melts at 219°. The *platinochloride* crystallises in long needles containing $6H_2O$. The *hydrobromide* crystallises in yellowish-brown needles, and softens at 126°, melting at a slightly higher temperature. The *hydrogen sulphate* separates from hot water in yellow, prismatic crystals. The *nitrate* crystallises in yellow needles.

When the hydriodide is treated with chloroform and caustic soda, an additive compound, $C_{22}H_{23}NO_4,CHCl_3$, is formed, which crystallises from chloroform in almost colourless tablets, melts at 162—163°, and does not lose weight at 100°. A compound with acetone was prepared in a similar manner but could not be obtained crystalline. This substance serves as a convenient source for the salts of the base, since it is readily decomposed by dilute acids, acetone and the corresponding salt of the base being produced. Dehydrocorydaline also appears to form a hydropolysulphide when its hydriodide is treated with yellow ammonium sulphide. The free base has been obtained in yellow crystals but only in extremely small quantity. When dehydrocorydaline is reduced, it is converted into a base which has the composition and melting point of corydaline and also gives many of the same reactions; it, however, forms a normal *aurochloride*,

$$C_{22}H_{27}NO_4,HAuCl_4 + 4H_2O,$$

which crystallises in slender, pale yellow prisms. Dehydrocorydaline, like corydaline itself, contains four methoxy-groups, and therefore has the formula $C_{18}H_{11}N(OMe)_4$.

Bulbocapnine is not acted on by iodine in a similar manner to corydaline. The methiodide melts at 235—240°, whereas Freund and Josephi give the melting point 257°. When treated with acetic anhydride, the alkaloid is converted into the *triacetyl* derivative,

$$C_{18}H_{13}N(OMe)(OAc)_3,$$

which crystallises in white needles and yields a crystalline *hydrochloride* and *platinochloride* which appear to have abnormal compositions.

Corycavine melts at 216—217° (214—215°, Freund and Josephi). It appears to have the formula $C_{23}H_{23}NO_6$, and not $C_{23}H_{23}NO_5$ as stated by Freund and Josephi; this also agrees with the composition of its salts. The *hydrochloride*, $C_{23}H_{23}NO_6,HCl$, crystallises in compact needles and the *platinochloride*, $(C_{23}H_{23}NO_6)_2,H_2PtCl_6 + 3H_2O$, in pale yellow granules. The alkaloid does not appear to be affected by iodine.

Corybulbine, $C_{21}H_{25}NO_4$, melts at 238—240°. The *hydrochloride* crystallises in yellowish prisms, and the *platinochloride* crystallises with $3H_2O$. Iodine acts on the base as it does on corydaline, but the product has not been obtained in sufficient quantity for analysis.

A. H.

Erythrophleïne. By ERICH HARNACK (*Arch. Pharm.*, 1896, **234**, 561—570).—The author has recently examined a sample of "*Erythrophleïn hydrochloricum*" prepared by E. Merck, which yields a base differing in several important points from that previously investigated (Harnack and Zabrocki, *Arch. exper. Path. Pharm.*, **15**). The question whether the alkaloid was in each case obtained from a parent bark of the same species (*Erythrophleum guineense*) remains unsettled.

The commercial hydrochloride is a fine, bright yellow, amorphous powder which is hygroscopic, and gradually agglomerates to a dry, solid mass when kept; it dissolves freely in cold water, and the solution has a tendency to froth. The base itself is precipitated by alkalis from the solution of the hydrochloride; it is freely soluble in alcohol and ether, soluble in amylic alcohol and ethylic acetate, and insoluble in light petroleum; its crystallisation has not been accomplished. The *platinochloride* and the *bismuthoiodide* are described and were analysed, but a decision could not be made between the formulæ $C_{28}H_{43}NO_7$ and $C_{28}H_{45}NO_7$ for the base.

When the hydrochloride of the base is heated with hydrochloric acid (38 per cent.) in a reflux apparatus, it undergoes hydrolysis, forming *erythrophleic acid*, $C_{27}H_{40}O_8$ or $C_{27}H_{42}O_8$, and methylamine; the acid is not decidedly crystalline. A. G. B.

Serum-albumin Crystals. By A. MICHEL (*Chem. Centr.*, 1896, i, 757—758, from *Verh. physiol. med. Ges. Würzburg*, **29**, No. 3, and *Centr. med. Wiss.*, 1896, 152—153).—The crystals were prepared from horse's blood serum. An equal volume of saturated solution of ammonium sulphate is added to the serum, and the globulin which is thus precipitated is filtered off. To the filtrate, ammonium sulphate solution is added until it just gets cloudy. The crystals of albumin sink, and are purified by repeatedly dissolving them in water and precipitating by ammonium sulphate; they are doubly-refracting, hexagonal prisms about a centimetre long; they are coagulated by heat at 51—53° without change of form, but their double refraction and solubility in water is lost. They contain C, 53·1; H, 7·1; N, 15·9; S, 1·9; O, 22, and ash, 0·22 per cent. The specific rotation is about −61°.

AUGUST GÜRBER adds a note that, among other animals, the blood-serum of the rabbit was the only one that yielded crystals. Crystals are best obtained from horse's serum, in which the amount of globulin is small. W. D. H.

Organic Chemistry.

Preparation of Tetramethylethylene. By IVAN KONDAKOFF (*J. pr. Chem.*, 1896, [2], **54**, 429—432).—Of the three methods for the preparation of tetramethylethylene, that of Baeyer and Thiele from pinacone is, in the author's opinion, the most convenient. The yield in this reaction is 25 per cent. less than the theory, the loss being mainly due to the formation of dihexylene and the acetate of dimethylisopropylcarbinol, the latter compound being produced by the action of the zinc bromide on the tetramethylethylene formed. J. F. T.

Action of Alcohols on Tetrachlorethylethylic Ether. By A. PERGAMI (*Gazzetta*, 1896, **26**, ii, 466—477).—Tetrachlorethylethylic ether, $CCl_3\cdot CHCl\cdot OEt$, prepared by Paternò's method (Abstr., 1873, 158) boils at 189·9° (corr.) under 756·9 mm. pressure. On heating it in a closed tube with primary isobutylic alcohol for 3 hours at 200—210°, and distilling the product in a current of steam, *ethylisobutyltrichloracetal*, $CCl_3\cdot CH(O\cdot CH_2\cdot CHMe_2)\cdot OEt$ is obtained; this is a colourless, limpid oil of characteristic ethereal odour, is very soluble in all ordinary solvents, but insoluble in alkalis, boils at 229·31° under 752·72 mm. pressure, has a sp. gr. = 1·186 at 22°, and the normal molecular weight in freezing acetic acid.

Anhydrous chloral readily combines with primary isobutylic alcohol with development of heat, giving a liquid *chloral isobutylate* boiling at about 130°, which, when treated first with phosphorus pentachloride, and then with water, is converted into *tetrachlorethylic isobutylic ether*, $CCl_3\cdot CHCl\cdot O\cdot CH_2\cdot CHMe_2$; it is a limpid oil of camphor-like odour, boils at 215·16° under 761·89 mm., has a sp. gr. of 1·332 at 0° and 1·324 at 27°, and the normal molecular weight in freezing acetic acid. When heated with primary isobutylic alcohol at 200—210° in a closed tube, it yields *di-isobutyltrichloracetal*,

$$CCl_3\cdot CH(O\cdot CH_2\cdot CHMe_2)_2,$$

which resembles its lower homologue in cryoscopic behaviour, boils at 241·75° under 759·57 mm. pressure, and has a sp. gr. of 1·139 at 0°, and 1·133 at 26°.

The tetrachlorether reacts less readily with secondary alcohols, and a poor yield of product is obtained, owing to the occurrence of secondary reactions. On heating secondary isobutylic alcohol with tetrachlorether at 160° for 3—4 hours, a small proportion of a *trichloracetal* of the constitution $CCl_3\cdot CH(O\cdot CHMeEt)\cdot OEt$ is obtained; it boils at 208—215°. If similarly treated, isopropylic alcohol yields a *trichloracetal* of the constitution $CCl_3\cdot CH(O\cdot CHMe_2)\cdot OEt$, which boils at 198—204°. The diethylic ether of glycerol, when heated with tetrachlorether, gave a small quantity of a *substance* boiling at 269—271°, which, however, could not be purified.

Tertiary alcohols do not react with tetrachlorether; on heating trimethylcarbinol with tetrachlorether at 140—150°, the latter decomposes, yielding Paternò's trichloracetal (*loc. cit.*) and chloral alcoholate.

W. J. P.

Action of Potassium Permanganate on the Polyhydric Alcohols and their Derivatives. By LÉON PERDRIX (*Compt. rend.*,

1896, **123**, 945—948).—The author has studied, quantitatively, the action of acidified potassium permanganate solution on the polyhydric alcohols at the boiling temperature. The four following equations are given for (1) glycol, (2) glycerol, (3) erythritol, and (4) mannitol.

$$(1)\ C_2H_6O_2 + 4O = CO_2 + CH_2O_2 + 2H_2O.$$
$$(2)\ C_3H_8O_3 + 5O = CO_2 + 2CH_2O_2 + 2H_2O.$$
$$(3)\ C_4H_{10}O_4 + 6O = CO_2 + 3CH_2O_2 + 2H_2O.$$
$$(4)\ C_6H_{14}O_6 + 8O = CO_2 + 5CH_2O_2 + 2H_2O.$$

For each addition, therefore, of the group CH·OH one more oxygen atom is required, and one more molecule of formic acid is produced. The amounts of oxygen required for the oxidation of certain atomic groups under the experimental conditions adopted are presented by the following equations.

(a) $CH{\cdot}OH + O = CH_2O_2$. (b) $CH_2{\cdot}OH + 2O = 0{\cdot}5CO_2 + 0{\cdot}5CH_2O_2 + H_2O$.
(c) $COOH + 0{\cdot}5O = CO_2 + 0{\cdot}5H_2O$. (d) $COH + 1{\cdot}5O = CO_2 + 0{\cdot}5H_2O$.
(e) $CO + O = CO_2$. (f) $CH_2 + 2O = CH_2O_2$.

Knowing the constitution of any given substance, the exact equation representing its oxidation can be constructed by reference to the above numbers, and will be found to agree with the results of experiment; dextrose is a case instanced in the paper. The monhydric alcohols are, however, exceptions to this rule. A. C. C.

The Two Optically Isomeric Methylmannosides. By Emil Fischer and Leo Beensch (*Ber.*, 1897, **29**, 2927—2931).—Methylmannoside can be formed from mannose by treating it with a strong methyl alcoholic solution of hydrogen chloride. It is, however, more conveniently prepared by means of a modified form of the glucoside synthesis, using an extremely dilute solution of hydrogen chloride in methylic alcohol.

Methyl-d-mannoside, prepared in this way from *d*-mannose, is anhydrous whether crystallised from water or from alcohol. It melts at 190—191° (193—194° corr.) without change, and is soluble in water to the extent of 30·7 parts in 100 at 15°; it has a sp. gr. = 1·473 at 7°/4°, and a rotation $[\alpha]_D^{20°} = +79{\cdot}2°$. The compound shows no tendency towards dimorphism, remaining unchanged after heating for 5 hours at 100°.

Methyl-l-mannoside, prepared from pure *l*-mannose by the same method, has identically the same melting point and crystalline form. Its rotation, $[\alpha]_D^{20°} = -79{\cdot}4°$.

Racemic methylmannoside possesses the property, which has been previously noticed in the case of sodium ammonium racemate, of crystallising unchanged from its aqueous solutions at higher temperatures, whilst at temperatures below 8° its two optically active components crystallise separately. On allowing the mannoside to crystallise at a temperature of about 15°, quadratic leaflets are obtained quite different in form from the optically active compounds; these melt at 165—166° (166·5—167·5° corr.). The sp. gr. determined in benzene = 1·443 at 7°/4°, and it is optically inactive in aqueous solution.

Below 8°, the *d*- and *l*-compounds crystallise separately, and can be separated mechanically. J. F. T.

Allotropy of Sucrose. By FERDINAND G. WIECHMANN (*J. Physical Chem.*, 1896, 1, 69—74).—Solid sugar is known to exist in two allotropic modifications, the crystalline and the amorphous. The amorphous variety is obtained by slowly melting the pure crystalline sugar, carrying the temperature to about 160°, and then allowing the melt to cool. Although this substance can be kept unchanged for some time, its condition seems an unstable one, and the tendency exists to return sooner or later to the crystalline form. To study this transformation more closely, the author prepared specimens of pure amorphous sugar, and of amorphous sugar containing traces of calcium oxide, sodium carbonate, or sodium hydrogen carbonate. These specimens were kept under observation for two months and a half. It was found that, in all the specimens of the pure sugar, no transformation into the crystalline form had occurred, but in all cases in which impurities had been added, a complete change into the crystalline modification had taken place. This was true of specimens which had been kept in the dark, as well as of those which had been exposed to daylight. Wherever crystallisation occurred, it was observed to start from one or more points, and to radiate from these points as centres, giving rise to perfectly circular forms. It seems that the minute amounts of foreign substance had, by their presence, imparted sufficient impulse to the sugar molecules to cause these to assume a more stable state of equilibrium in the crystalline modification. H. C.

Chemical Syntheses by Aid of the Dark Electric Discharge. By SIMA M. LOSANITSCH and MILORAD Z. JOVITSCHITSCH (*Ber.*, 1897, 30, 135—139).—The experiments were carried out in a Berthelot ozoniser, which the authors propose to term an *electriser*. The apparatus was attached to a manometer containing water or mercury, by means of which any contraction could be observed. A current of 3—5 ampères and 70 volts was employed. Under these circumstances, carbonic oxide and water yield formic acid, whilst carbonic anhydride and water yield formic acid and oxygen, the latter then converting a part of the water into hydrogen peroxide. Carbonic oxide and hydrogen yield formaldehyde, which polymerises. Carbonic anhydride and hydrogen yield formic acid. Carbonic oxide and methane react in equal volumes to form acetaldehyde, which, however, polymerises. Carbonic oxide and sulphuretted hydrogen yield sulphur and a reducing substance which is probably thioformaldehyde. Contraction takes place in the reaction between carbonic oxide and hydrogen chloride, probably with formation of formic chloride. Carbonic oxide and ammonia rapidly combine to form formamide, a small amount of hydrogen cyanide being produced at the same time. Carbon bisulphide and hydrogen form hydrogen sulphide and a dark-coloured solid substance, which the authors state to be carbon monosulphide; this substance, together with carbon oxysulphide, is also formed by the action of carbonic oxide on carbon bisulphide. Nitrogen and water form ammonium nitrite, as had previously been found by Berthelot. Unsaturated hydrocarbons are converted into polymeric substances. Thus ethylene yields a thick, yellow liquid which boils above 200°. Benzene gives a thick, sticky, strongly-smelling mass. A. H

New Method of preparing Anhydrides. By GIUSEPPE ODDO and C. MANUELLI. (*Gazzetta*, 1896, **26**, ii, 477—484).—Many dibasic acids, in neutral or feebly alkaline aqueous solution, are converted into their anhydrides by acetic anhydride under certain conditions, the principal of which concern the distance between two carboxyl groups or between a carboxyl group and a carbon atom attached to another radicle such as hydroxyl, amidogen, or nitrilic nitrogen. 1 : 4-Dibasic acids are immediately precipitated from solutions of their barium salts as anhydrides on adding the theoretical quantity of acetic anhydride; phthalic and succinic acids are thus converted, but not isophthalic or terephthalic, oxalic or malonic acids. Salts of 1 : 4-dicarboxylic acids, such as methylsuccinic acid, which contain alkylic groups, are similarly converted into anhydrides, but if, like hydroxy-, dihydroxy-, or amidosuccinic acid or 3-nitrophthalic acid, they contain negative radicles, the anhydride is not formed. An exception is found in the case of naphthalene-1 : 1′-dicarboxylic acid, which readily yields the anhydride; it is of interest to note that camphoric acid is readily converted into its anhydride by the method now described.

Propionic, palmitic, benzoic, cinnamic, and the three nitrobenzoic acids are not thus converted into anhydrides; ortho- and para-amidobenzoic acids are converted into their acetates, whilst the meta-isomeride yields the acetyl derivative. Orthocyanobenzoic acid yields phthalimide, but its meta-isomeride remains unaffected; camphoric mononitrile gives its anhydride.

The explanation of the reaction is evidently that acetic anhydride acts on the salt, forming an unstable mixed anhydride, which then decomposes into the two simple anhydrides. W. J. P.

Composition of Wool-fat. By L. DARMSTAEDTER and ISAAC LIFSCHÜTZ (*Ber.*, 1896, **29**, 2890—2900. Compare Abstr., 1896, i, 522.) —When the soap produced by the hydrolysis of wool-fat is treated with cold alcohol, it yields a solution containing myristic and carnaubic acids, together with three new acids, only one of which has as yet been carefully examined. This acid, to which the authors give the name of *lanopalmic acid*, has the formula $C_{16}H_{32}O_3$, melts at 87—88°, and solidifies in radiating crystals. The melted acid very readily emulsifies with water; it is insoluble in aqueous alkalis, but dissolves in the presence of a little alcohol. The potassium salt appears to be stable in the presence of water, only when the solution is hot, decomposing, as the liquid cools, into an insoluble acid salt and free alkali.

The neutral alcohols from wool-fat have also been further examined, and the presence of unaltered fat, cholesterol and a number of new alcohols has been recognised.

Cerylic alcohol, $C_{27}H_{56}O$, crystallises with $6H_2O$, melts at 77—78°, and loses its water of crystallisation at a slightly higher temperature. It appears to contain a small quantity of a second alcohol, which melts at 69—70°, and is left behind when the mixture is oxidised with chromic acid. The cerylic alcohol is converted by oxidation into cerotic acid.

Carnaubylic alcohol, $C_{24}H_{50}O$, is more readily soluble in alcohol than the foregoing compound; it melts at 68—69°, and is converted by oxidation into carnaubic acid. When this alcohol is crystallised from

aqueous alcohol, it dries to a white, transparent mass, which contains 73·3 per cent. of water. A. H.

Compounds of Alloxan and Dimethylalloxan with Semicarbazide. By OTTO BROMBERG (*Ber.*, 1897, **30**, 131—134).—*Alloxansemicarbazide*, $C_5H_9N_5O_6$, is formed by direct union when aqueous solutions of alloxan and semicarbazide hydrochloride are mixed; it crystallises in broad, colourless needles, which gradually decompose when heated. It dissolves in dilute alkalis, but is gradually decomposed by them; when heated with dilute acids, it is converted, with loss of the elements of water, into *anhydroalloxansemicarbazide*, $C_5H_7N_5O_5$, which crystallises in slender, colourless needles; it is also gradually decomposed when heated alone. It dissolves in alkalis, reduces Fehling's solution, and when treated with hydrochloric acid and potassium chlorate, gives a solution which yields the murexide reaction, so that it is probably a derivative of alloxan, and not of alloxanic acid. Dimethylalloxan reacts with semicarbazide hydrochloride, with elimination of the elements of water, forming *dimethylalloxansemicarbazide*, $C_7H_{11}N_5O_5$; this crystallises in oblique, pointed tablets, and gradually decomposes when heated. Dilute acids convert it, with loss of a second molecule of water, into *anhydrodimethylalloxansemicarbazide*, $C_7H_9N_5O_4$; this is also formed when dimethylalloxan and semicarbazide hydrochloride are boiled together in aqueous solution. It crystallises in slender, six-sided plates, and, like the other compounds, decomposes gradually when heated. Aqueous alkalis convert it into a *substance*, $C_6H_{11}N_5O_3$, which crystallises in slender, colourless needles, decomposes at about 270°, and yields a crystalline sodium salt. The constitution of these compounds has not yet been ascertained. A. H.

Mesitylene from Acetone. By AD. LUCAS (*Ber.*, 1896, **29**, 2884—2887).—The conclusion of V. Meyer and Molz (this vol., i, 142) is confirmed, that mesitylene, formed by condensation from acetone, contains no isomeric trimethylbenzene. The action of sulphuric acid brings about no molecular transformation. as it is found that, when pure mesitylene is sulphonated and then regenerated from the sulphonic acid, it boils at exactly the same temperature as before. It is known, however, that some 1 : 2 : 3 : 4-trimethylbenzoic acid is formed when mesitylene is caused to condense with acetic chloride in the presence of aluminium chloride, and the product is oxidised. A partial molecular transformation must, therefore, have resulted from the action of the acetic chloride.

Commercial mesitylene contains very little impurity, although when distilled it passes over within a fairly wide interval of temperature. Such impurity as it does contain is of the nature of an olefine, for it unites directly with bromine in the cold. C. F. B.

Technical Uses of Ortho- and Para-nitrophenol. By LUDWIG PAUL (*Zeit. angw. Chem.*, 1896, 587—595).—The author finds that the preparation of orthonitrophenol from the corresponding sulphonic acid, by means of superheated steam, is not to be recommended for use on a commercial scale, on account of the poor yield (some 25 per cent.). The conversion of orthonitrophenol into orthonitranisoil, by heating it

with methylic chloride under pressure, is described, and also the conversion of the nitranisoil into dianisidine.

The author has also attempted to prepare diphenetidine and dianisidine from paraphenolsulphonic acid. This was first nitrated, and the orthonitrophenolparasulphonic acid thus obtained was converted into its methylic ether, the sodium salt of which is readily soluble in 80 per cent. alcohol. The corresponding ethylic ether, when distilled with superheated steam, gave orthonitrophenol, and not orthonitranisoil. When reduced with stannous chloride in acid solution, the ethylic ether was converted into phenetidinesulphonic acid, but on reduction with zinc dust in alkaline or acid solution, ethoxyazobenzenedisulphonic acid,

$$N_2[C_6H_3(OEt)\cdot SO_3H]_2,$$

was formed. The latter, on further reduction with stannous chloride and hydrochloric acid, yielded phenetidinemetadisulphonic acid, and this, when heated with water under pressure at 170° gave the corresponding monosulphonic acid. Directions are also given for the reduction of orthonitrophenol to the corresponding amidophenol on the large scale, by means of hydrogen sulphide, or on the small scale by means of stannous chloride; also of paranitrophenol to paramidophenol, by means of sodium sulphide and hydrogen chloride in the presence of tin. The preparation of paranitrophenetoil, of paramidophenetoil, and of phenacetin, are also described. J. J. S.

Mono- and Di-chloroparacresols. By GIROLAMO MAZZARA and MANFREDO LAMBERTI-ZANARDI (*Gazzetta*, 1896, **26**, ii, 399—403).—Paracresol is readily acted on by sulphuryl chloride, either alone or in chloroform solution, and after warming and adding sodium carbonate, the product yields 3-chloro-1 : 4-cresol [Me = 1], on distillation in a current of steam (Schall and Dralle, Abstr., 1885, 145). With two molecular proportions of sulphuryl chloride, Claus and Riemann's 2 : 5-dichloro-1 : 4-cresol is obtained (Abstr., 1883, 1111).

The authors consider that these facts show that the conclusions of Peratoner and Finocchiaro (Abstr., 1894, i, 368), and of Peratoner and Genco (Abstr., 1895, i, 342), are unwarranted. The phenols do not react with sulphuryl chloride in the ketonic form, and sulphuryl chloride cannot be applied to the diagnosis of phenolic hydroxyl. W. J. P.

Monochlorothymol and Dichlorocymene. By O. BOCCHI (*Gazzetta*, 1896, **26**, ii, 403—406).—Thymol and sulphuryl chloride react readily in molecular proportion, yielding *monochlorothymol*,

$$CMe\begin{matrix}\diagup CH{=\!=}CCl\diagdown \\ \diagdown CH\cdot C(OH)\diagup\end{matrix}CPr\,;$$

on treating the product with warm, dilute potash, separating the clear liquid, and treating with dilute sulphuric acid, solid chlorothymol is obtained; it crystallises from light petroleum in transparent, rhombic plates, melting at 58—60°. The *acetyl* derivative, $C_{14}H_{12}ClO_2$, obtained by the action of acetic anhydride on the chlorothymol, is a colourless liquid, whilst the *benzoyl* derivative, $C_{17}H_{17}ClO_2$, prepared by heating a potash solution of chlorothymol with benzoic chloride on the water bath, forms tetragonal crystals melting at 71—73°.

On gradually heating a mixture of chlorothymol with phosphorus pentachloride to 230°, reaction occurs, and on treating the product with

sodium carbonate, and distilling in a current of steam, the dichlorocymene, $CMe\lessgtr^{CCl:CH}_{CH\cdot CCl}\gtrdot CPr$, prepared by von Gerichten (Abstr., 1878, 570), is obtained; it boils at 240—243° (corr.), and its constitution is established by the fact that it yields paradichloroterephthalic acid when heated with dilute nitric acid at 180—200° in a closed tube.

W. J. P.

Blue Dye from Quinone. By JAMES LEICESTER (*Chem. News*, 1896, 74, 236).—*Dinitrodianilidoquinone*, $C_{18}H_{12}N_4O_6$, probably

$$C_6H_2O_2(NH\cdot C_6H_4\cdot NO_2)_2,$$

obtained by heating benzoquinone in glacial acetic acid solution with orthnitraniline; it melts at 305°. When reduced by means of alcoholic ammonium sulphide, it yields a dark green powder, $C_{18}H_{10}N_4O_2$, called *istarine* which dissolves in acetic acid with an intense blue colour, red by reflected light, and dyes silk and wool a fast blue. Dilute sulphuric acid produces a strong fluorescence in the acetic acid solution.

D. A. L.

Fate of Cholesterol in the Animal Organism. By STANISLAS BONDZYŃSKI and V. HUMNICKI (*Zeit. physiol. Chem.*, 1896, 22, 396—416). (For the physiological part of this paper, see this vol., ii, 153).—*Coprosterol*, $C_{27}H_{48}O$, is formed by the passage of cholesterol through the body; it crystallises in long, slender needles, melts at 95—96° and has $[\alpha]_D = +24°$. It gives reactions similar to those of cholesterol, of which it seems to be the dihydro-derivative. The *acetyl* derivative forms needles, and melts at 85°; the *bromacetyl* derivative is crystalline, and melts at 118°; the *propionyl* derivative crystallises in needles melting at 92°; the *benzoyl* derivative forms rectangular plates, melting at 114—115°. The *cinnamoyl* derivative crystallises in rectangular prisms, melts at 169°, and yields a crystalline *dibromide* melting at 165—166°. *Cinnamoylcholesterol*, prepared for purposes of comparison, crystallises in characteristic tablets, melts at 149°, and yields a *tetrabromide* melting at 139°.

Hippocoprosterol, $C_{27}H_{54}O$ or $C_{27}H_{56}O$, is obtained from the faeces of the horse; it forms microscopic needles, and melts at 74—75°.

W. D. H.

Hæmosterol, a New Constituent of Blood. By KARL HÜRTHLE (*Chem. Centr.*, 1896, i, 562; from *Schles. Ges. f. vaterländ. Kult. Med. Sekt.*, 1895).—The author has isolated a new compound, *hæmosterol*, from the fresh blood of various animals, in which it is present to the amount of about 0·1 per cent., and also from blood serum. It crystallises in optically uniaxial needles, which melt at 37—42°, and the molten mass, on cooling, shows a blue fluorescence. It is easily soluble in ether and chloroform and slightly so in hot alcohol. Solutions of the crystals are lævorotatory. To this substance, the author ascribes the formula $C_{20}H_{31}(OH)$, and regards it as allied to cholesterol, the characteristic reactions of which it gives with slight variations. Attempts to obtain benzoyl derivatives were unsuccessful. Three different substances, containing respectively 80, 82, and 84 per cent. of carbon, and melting at 37—46°, were obtained from the blood serum of horses.

E. W. W.

Paranitrobenzyl Bases. By CARL PAAL & HERMANN SPRENGER (*Ber.*, 1897, **30**, 61—70).—These were prepared, in the case of the methyl-, ethyl-, and propyl-amine derivatives, by heating paranitrobenzylic chloride with a 33 per cent. aqueous solution of the amine for 2 hours in a sealed tube at 110—120°; in the case of the *i*-amylamine, allylamine, and aniline derivatives, by boiling a concentrated alcoholic solution of the chloride and the amine in a reflux apparatus. In the first cases, a tertiary base is the chief product, the secondary base being formed in smaller quantity, even when a large excess of the amine is used; in the other cases, the secondary base is formed in larger quantity. The two products are easily separated, as the tertiary amine has but very feebly basic properties, whereas the secondary amine forms stable salts.

Paranitrobenzylmethylamine, $NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}NHMe$, is a yellow syrup; the *hydrochloride* melts at 219°, the yellowish-red *platinochloride* at 220°, and the oxalate at 188°. *Bis-paranitrobenzylmethylamine*, $(NO_2{\cdot}C_6H_4{\cdot}CH_2)_2NMe$, forms yellow needles melting at 104°.

Paranitrobenzylethylamine, $NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}NHEt$, is a yellow, syrupy oil; the *hydrochloride* and *oxalate* melt at 226° and 207° respectively. The reddish-yellow *platinochloride* was also prepared. *Bis-paranitrobenzylethylamine*, $(NO_2{\cdot}C_6H_4{\cdot}CH_2)_2NEt$, crystallises from ether in orange-red crystals resembling rhombohedra; from alcohol, in yellow plates that melt at 68°.

Paranitrobenzylpropylamine, $NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}NHPr$, is a yellow syrup; the *hydrochloride* melts at 225°, the yellow *platinochloride* at 177°, and the *oxalate* at 228°. *Bis-paranitrobenzylpropylamine*,

$$(NO_2{\cdot}C_6H_4{\cdot}CH_2)_2NPr,$$

is yellow, and melts at 77°.

Paranitrobenzylisoamylamine, $NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}NH{\cdot}C_5H_{11}$, forms a yellow syrup; the *hydrochloride* melts at 204°, the orange *platinochloride* at 206°, the *oxalate* at 223°, and the yellow *picrate* at 144°. The base itself is reduced by zinc dust and acetic acid, at a temperature not exceeding 30°, to *paramidobenzylisoamylamine*,

$$NH_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}NH{\cdot}C_5H_{11},$$

an unstable oil. *Bis-paranitrobenzylisoamylamine*,

$$(NO_2{\cdot}C_6H_4{\cdot}CH_2)_2N{\cdot}C_5H_{11},$$

is yellow, and melts at 57°.

Paranitrobenzylallylamine, $NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}NH{\cdot}C_3H_5$, is a yellow oil; the *hydrochloride* melts at 226°, the reddish-yellow *platinochloride* at 174°, the *oxalate* at 224°, and the yellow *picrate* at 146°. *Bis-paranitrobenzylallylamine*, $(NO_2{\cdot}C_6H_4{\cdot}CH_2)_2N{\cdot}C_3H_5$, is yellowish, and melts at 46°.

Paranitrobenzylaniline, $NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}NHPh$, is orange-coloured, and melts at 72°; it is reduced by iron filings and acetic acid to *paramidobenzylaniline*, $NH_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}NHPh$, a yellow oil which deposited a few crystals melting at 49—50°, and yields a yellow, granular, amorphous *hydrochloride* (with 2HCl). *Bis-paranitrobenzylaniline*, $(NO_2{\cdot}C_6H_4{\cdot}CH_2)_2NPh$, is greenish-yellow, and melts at 169°.

C. F. B.

Action of Orthonitrobenzylic Chloride on Hydroxylamine. By CARL PAAL and H. POLLER (*Ber.*, 1897, **30**, 58—60).—When ortho-

nitrobenzylic chloride is heated with hydroxylamine in alcoholic solution, yellow crystals of *bis-orthonitrobenzylhydroxylamine*,

$$(NO_2\cdot C_6H_4\cdot CH_2)_2N\cdot OH,$$

are obtained, in addition to an oil which is possibly the mono-derivative. The crystals melt at 124° ; the *hydrochloride* is decomposed by water ; the *acetyl* derivative melts at 134° ; reduction with zinc dust and alcoholic hydrochloric acid at a temperature not exceeding 40°, leads to the formation of *bis-orthamidobenzylhydroxylamine*,

$$(NH_2\cdot C_6H_4\cdot CH_2)_2N\cdot OH,$$

melting at 142°, and treatment with hydrochloric acid and sodium nitrite, in alcoholic solution, to yellow *orthonitrobenzylorthonitroisobenzaldoxime*, $NO_2\cdot C_6H_4\cdot CH_2\cdot N\!<\!\overset{O}{\underset{CH\cdot C_6H_4\cdot NO_2}{|}}$, melting at 150°.

C. F. B.

The "Diazo" Controversy. By CHRISTIAN W. BLOMSTRAND (*J. pr. Chem.*, 1896, [2], **54**, 305—339).—An historical and critical account of the recent work of Hantzsch and of Bamberger on the constitution of the diazo-compounds.

J. F. T.

Diazosulphonates and Free Diazosulphonic Acids. By ARTHUR R. HANTZSCH and M. SCHMIEDEL (*Ber.*, 1897, **30**, 71—88. Compare Abstr., 1895, i, 180).—Potassium *syn*-diazosulphonates are obtained by dissolving or suspending the amine in water and hydrochloric (or occasionally sulphuric) acid, diazotising the well-cooled solution with sodium nitrite, and pouring the mixture into a well-cooled solution of potassium sulphite. They vary in colour from light to dark orange ; some can be dried on a porous plate over phosphoric anhydride in the dark ; others at once undergo a molecular transformation under these circumstances, and even explode spontaneously ; the darker-coloured salts seem to be less stable than the lighter ones. In aqueous solution, even at 0°, they are all transformed into the stereoisomeric *anti*-diazosulphonates, but with very varying rapidity. The *syn*-diazosulphonate of orthochlorobenzene is comparatively stable, as is also that of 2 : 4-di-iodobenzene ; those of parachloro-, parabromo-, and 2 : 4-dibromo-benzene are less stable ; whilst those containing an alkyl group, such as the salts of para- and meta-toluene, of xylene, pseudocumene, mesitylene, and orthanisidine, are so unstable that it is impossible to isolate a pure *syn*-salt, and the same is true even of dibromoparatoluene and dibromorthotoluene, which also contain halogen atoms. The *syn*-diazosulphonate of sulphanilic acid was only obtained in solution. Lastly, the *syn*-diazosulphonates of tribromobenzene and naphthalene (α and β) cannot be made to yield *anti*-salts ; in the last two cases, $\alpha\alpha$- or $\beta\beta$-azonaphthalene is respectively formed. To prepare an *anti*-salt, the *syn*-salt is suspended in about 30 times its weight of water, and the solution allowed to remain at the ordinary temperature for an hour, during which time it is frequently shaken ; it is then boiled, and more water added, if necessary, to dissolve the salt ; the *anti*-salt crystallises out as the solution cools. These *anti*-salts are yellow or reddish-yellow in colour ; with barium chloride and silver nitrate, they yield respectively barium and silver salts that are sparingly

soluble in water. The potassium *syn*-diazosulphonates do not yield precipitates of such salts; on the other hand, unlike the *anti*-salts, they condense with β-naphthol and similar substances, forming azo-dyes.

Since the potassium *syn*-diazosulphonates can be titrated with iodine just as if they were sulphites, whilst the *anti*-salts do not act on iodine, the rate of transformation of *syn*- into *anti*-salt in an aqueous solution can be measured (usually at 0°) by titrating, from time to time, an aliquot portion of the solution with iodine. In the case of *syn*-diazobenzenesulphonate, about 10 per cent. is converted in the first minute; in the case of the orthochloro- or 2 : 4-di-iodo-benzene salts, only about 80 per cent. was converted at the end of a quarter of an hour. The reaction is not so simple as it seems, for the amounts transformed do not agree with those calculated on the assumption that the amount transformed at any time is proportional to the concentration of the unchanged substance at that time; the rate of transformation diminishes as the transformation proceeds.

The free *antidiazosulphonic acids* of *parabromobenzene*, 2:4-*dibromobenzene*, and *paratoluene* were obtained by suspending the silver anti-salts in water, decomposing them with the calculated quantity of hydrochloric acid, filtering, and allowing the filtrate to evaporate over sulphuric acid at a low temperature. They form yellow, deliquescent needles, and are all unstable; the last melts at 112—114°. C. F. B.

Action of Potassium Sulphite on Nitrodiazonium Salts. By ARTHUR R. HANTZSCH and H. BORGHAUS (*Ber.*, 1897, **30**, 89—92. Compare Bamberger and Kraus, Abstr., 1896, i, 610).—The isomeric nitrobenzenediazonium salts, chlorides as well as nitrates, are extremely unstable. With potassium sulphite, they yield yellow *syn*-diazosulphonates; these explode, even when moist; when allowed to remain in contact with aqueous potassium carbonate, they are transformed into the *anti*-salts; and when treated with an excess of potassium sulphite, they yield hydrazinedisulphonates, $NO_2\cdot C_6H_4\cdot N(SO_3K)\cdot NH\cdot SO_3K$, from which boiling with dilute hydrochloric acid sets free the hydrazines.

Paranitrobenzenediazosulphonic acid can be obtained in red, efflorescent, unstable crystals by treating the yellow anti-silver salt (which explodes at 140—141°) with the calculated amount of hydrochloric acid, and evaporating the filtrate at 0° under diminished pressure.

Potassium metanitrobenzenesyndiazosulphonate is extremely unstable, exploding even when moist and at 0°; the *anti*-salt is yellow. *Potassium metanitrophenylhydrazinedisulphonate* crystallises with $2H_2O$, and is red; recrystallisation from water converts it gradually into a yellow salt, apparently $NO_2\cdot C_6H_4\cdot NH\cdot NH\cdot SO_3K + H_2O$.

The *orthonitrobenzene* derivatives resemble the above in properties.

Diazosulphonates of dinitrophenol and of two nitrotoluenes were also prepared; the first crystallises in yellow plates or red needles, apparently with $2H_2O$ in both cases; the last two call for no particular remark. C. F. B.

Bis-Diazonium Salts. By ARTHUR R. HANTZSCH and H. BORGHAUS (*Ber.*, 1897, **30**, 92—93).—Paraphenylenediamine yields the yellowish, very explosive *bisdiazonium chloride*, $C_6H_4(N_2Cl)_2$, when treated with nitrogen trioxide in hydrochloric acid solution at 0°; the

sulphate is more stable. Metaphenylenediamine also yields similar derivatives; orthophenylenediamine does not. Attempts to convert these salts into cyanides or sulphonates were unsuccessful, they are completely decomposed. C. F. B.

Oximes of the Fatty Aromatic Ketones containing the higher Alkyls. The Stereochemistry of Nitrogen. By ADOLPH CLAUS and HERMANN HÄFELIN (*J. pr. Chem.*, 1896, [2], **54**, 391—405).—Further instances are brought forward tending to show that, contrary to van't Hoff's law, oximes containing a fatty and an aromatic group on the carbon atom of the oxime residue do not exist in two forms.

Metaxylyl heptadecyl ketone, (*4-stearometaxylone*),

$$C_6H_3Me_2\cdot CO\cdot C_{17}H_{35}\ [Me_2 : CO = 1 : 3 : 4],$$

is prepared from metaxylene and stearic chloride in the presence of aluminium chloride; when recrystallised from alcohol, it forms white, vitreous plates melting at 39°, distils at 260—280° under 15 mm. pressure, and yields 2 : 4-dimethylbenzoic acid (m. p. 126°) on oxidation with dilute nitric acid. This compound, like all ketones of this class, expands on solidifying.

Metaxylyl heptadecyl ketoxime, prepared in the usual way, separates from solvents as an oil which solidifies on standing; it melts at 45°, and is quantitatively hydrolysed when heated with hydrochloric acid at 125—130°.

On treatment with phosphorus pentachloride or sulphuric acid, the oxime undergoes the Beckmann rearrangement, being converted into *stearylmetaxylidide*, $C_6H_3Me_2\cdot NH\cdot CO\cdot C_{17}H_{35}$, which can also be prepared from stearic chloride and metaxylidine. It melts at 95° after recrystallisation from alcohol, and as on hydrolysis it yields only stearic acid and metaxylidine, it must be homogeneous. If the theoretical stereochemical form really existed, it should give, on rearrangement and hydrolysis, xylenecarboxylic acid and heptadecylamine; no trace of these, however, could be found.

Phenyl heptadecyl ketone (*stearophenone*), $C_6H_5\cdot CO\cdot C_{17}H_{35}$, prepared in the same way, crystallises from alcohol in snow-white leaflets, melts at 59°, and distils at 250—270° under 18 mm. pressure. The *oxime* crystallises from the same solvent in small leaves melting at 53°, and on rearrangement yields the anilide of stearic acid, melting at 93°.

Paraxylyl heptadecyl ketone, (*2-stearoparaxylone*),

$$C_6H_3Me_2\cdot CO\cdot C_{17}H_{35}\ [Me_2 : CO = 1 : 4 : 2],$$

from paraxylene and stearic chloride, crystallises from alcohol in colourless leaflets melting at 57°. The *oxime*, like the meta-compound separates from solvents as an oil, which solidifies after a time; it melts at 50°. No trace of paraxylenecarboxylic acid could be obtained on rearrangement and hydrolysis.

Similarly, *paratolyl heptadecyl ketoxime*, which crystallises from alcohol in glistening needles, melting at 64°, and *paratolylpentadecyl ketoxime* gave only stearylparatoluide and palmitylparatoluide respectively on rearrangement and hydrolysis.

Mesityl pentadecyl ketone, (*palmitomesitone*), $C_6H_2Me_3\cdot CO\cdot C_{15}H_{31}$ $[Me_3 : CO = 1 : 3 : 5 : 2]$, formed from mesitylene and palmitic chloride in the presence of aluminium chloride, crystallises from alcohol in white

leaflets, melts at 35°, and distils at about 280° under 15 mm. pressure. Like all known ketones containing a mesityl residue, it does not yield an oxime with hydroxylamine. J. F. T.

A Curious Instance of Molecular Rearrangement. By LUDWIG CLAISEN (*Ber.*, 1897, **29**, 2931—2933).—Like acetone, acetophenone condenses with ethylic orthoformate, with the formation of *acetophenone orthodiethylic ether*, $CMePh(OEt)_2$, a compound which distils unchanged at 107° under a pressure of 17 mm., but when distilled under atmospheric pressure, it loses the elements of a molecule of alcohol, and passes into *iso-acetophenone ethylic ether*, $OEt·CPh:CH_2$, an oil boiling at 209°. If this be now slightly superheated (that is, boiled for some hours under a pressure of 2 atmospheres), rearrangement ensues with the production of phenyl propyl ketone, $CH_2:CPh·OEt = COPh·CH_2Et$.

In the same way, phenyl ethyl ketone can be prepared from acetophenone orthodimethylic ether, and phenyl butyl ketone from the orthodipropylic ether. Benzophenone also, on treatment with methylic orthoformate, yields *benzophenone orthodimethylic ether*, $CPh_2(OMe)_2$, melting at 107°, and with ethylic orthoformate, *benzophenone orthodiethylic ether*, melting at 52°.

The ketone ortho-ethers yield ketoneanilides when boiled with aniline. The *anilide of acetone*, $CMe_2:NPh$, is a liquid boiling at 195°, whilst the *anilide* of *acetophenone*, $CMePh:NPh$, is a solid melting at 41°, and boiling without decomposition at 310°.

From pyruvic acid, the following compounds can be obtained on condensation with ethylic orthoformate. *Ethylic a-diethoxypropionate*, $CMe(OEt)_2·COOEt$, an oil boiling at 191°, which on treatment with phosphoric anhydride passes into *ethylic a-ethoxyacrylate*,

$$CH_2:C(OEt)·COOEt,$$

boiling at 180°, and this on hydrolysis yields *a-ethoxyacrylic acid*, $CH_2:C(OEt)·COOH$, crystallising in glistening needles, and melting at 62°. This acid is quite different from the *a*-ethoxyacrylic acid, melting at 108°, obtained by Otto from *aa*-dichloropropionic acid, and by Merz from *aa*-dibromopropionic acid. The two compounds must necessarily be *a*-ethoxyacrylic acids, and this is, therefore, an interesting instance of isomerism, which is not capable of explanation according to the existing theories. Ethylic orthoformate combines with all aldehydes, both fatty and aromatic, with the production of compounds of which several are still under investigation. J. F. T.

Electrolytic Reduction of Aromatic Nitro-compounds. By LUDWIG GATTERMANN (*Ber.*, 1896, **29**, 3034—3037. Compare Abstr., 1893, i, 566, and Abstr., 1894, i, 72, 502).—[With A. E. LOCKHART 5 : 2-*Amidohydroxyacetophenone* is obtained by electrolytic reduction of metanitroacetophenone, and crystallises from water in golden-yellow leaflets melting at 110° ; the aqueous solution develops a brownish-red coloration with ferric chloride, and the alkaline solutions are intensely yellow, becoming dark brown on exposure to air.

[With C. WEINLIG] 5:2-*Amidohydroxybenzophenone* is obtained from metanitrobenzophenone ; it crystallises from water in orange-coloured plates, and melts at 107°.

5:2-*Amidohydroxyphenyl paratolyl ketone*, obtained by reducing metanitrophenyl paratolyl ketone; crystallises from water in golden-yellow needles, and melts at 93°. M. O. F.

Electrolytic Reduction of Aromatic Nitro-compounds. By LUDWIG GATTERMANN [and ALWAY] (*Ber.*, 1896, **29**, 3037—3040. Compare foregoing abstract).—When paranitrobenzaldehyde is submitted to electrolytic reduction, the *compound* $COH\cdot C_6H_4\cdot N{<}{\overset{O}{\underset{CH\cdot C_6H_4\cdot NO_2}{|}}}$, is produced; it crystallises from pyridine in yellow needles melting at 224°. *Paranitrosobenzaldehyde*, which is obtained on oxidising this substance with ferric chloride, crystallises from glacial acetic acid in yellow needles, and melts to a green liquid at 137—138°.

Metanitrobenzaldehyde also yields, on reduction, a *compound*,

$$COH\cdot C_6H_4\cdot N{<}{\overset{O}{\underset{CH\cdot C_6H_4\cdot NO_2}{|}}},$$

which crystallises from pyridine in greyish-yellow aggregates, and melts at 191°; oxidation with ferric chloride converts it into metanitrosobenzaldehyde (compare Bamberger, Abstr., 1895, i, 217). M. O. F.

Electrolytic Reduction of Aromatic Nitro-compounds. By LUDWIG GATTERMANN [WÜRST and BOHN] (*Ber.*, 1896, **29**, 3040—3042. Compare foregoing abstracts).—When nitrobenzene is submitted to electrolytic reduction in presence of benzaldehyde, the benzylidene derivative of phenylhydroxylamine (Abstr., 1894, i, 412) is produced. The *benzylidene* derivatives of ortho-, meta-, and para-tolylhydroxylamine melt at 119—120°, 95—96°, and 123—124° respectively; the *benzylidene* derivative of paraxylylhydroxylamine crystallises from petroleum in colourless needles, and melts at 129—130°.

The *benzylidene* derivative of metahydroxylamidobenzoic acid is obtained from metanitrobenzoic acid and benzaldehyde; it melts and decomposes at 200°. M. O. F.

Action of Hydroxylamine on Benzylideneacetophenone. By ADOLPH CLAUS (*J. pr. Chem.*, 1896, [2], **54**, 405—414).—The true oxime of benzylideneacetophenone is in no case formed when hydroxylamine acts on the ketone, but at the moment of its formation it either undergoes an intramolecular transposition, or combines again with another molecule of the hydroxylamine. In the first case, the product has the same composition as the true oxime, but none of the reactions characteristic of an oxime; whilst in the second, two products are formed, which, although they behave as oximes, have a different empirical formula from the true oxime.

All three compounds are always obtained when hydroxylamine acts on the ketone; they can be separated in the following way.

I. Water is added to the strongly alkaline mixture until a precipitate is no longer produced; the precipitate, after repeated recrystallisation from alcohol, melts at 73°, and is evidently *αγ-diphenyldihydroisoxazole* since, it is readily converted into αγ-diphenylisoxazole on oxidation with chromic acid in acetic acid solution.

II. On neutralising the alkaline filtrate with hydrochloric acid, a precipitate is produced consisting of two substances, which can be separated by treatment with hot benzene. The insoluble portion separates from alcohol in fine, colourless crystals, melting at 218°, whilst that dissolved by the hot benzene crystallises out on cooling in slender needles, melting at 150°. They both behave similarly, yielding acetyl compounds with acetic anhydride, and isoxazole on oxidation; they are also isomeric. A further description of their properties is reserved.

3:5-*Diphenylisoxazole* is obtained as described above. It is a very stable compound crystallising in colourless glistening leaflets melting at 140°. J. F. T.

Calcium Orthoethylbenzoate, and the author's Theory of Water of Crystallisation. By THEODOR SALZER (*Ber.*, 1897, **30**, 103—104).—Calcium orthoethylbenzoate is described by Giebe (this vol., i, 62) as containing $3H_2O$, whereas, according to the author's theory, it should only crystallise with $2H_2O$ (Abstr., 1896, ii, 415). On examination, the salt was found to contain a small amount of some acid of lower molecular weight, and, after five recrystallisations, separated out with only $2H_2O$. A. H.

Preparation of Mandelic Acid. By CARL PAPE (*Chem. Zeit.*, 1896, **20**, 90).—Mandelonitrile is readily obtained by mixing an aqueous solution of the sodium hydrogen sulphite compound of benzaldehyde with a concentrated aqueous solution of potassium cyanide. The nitrile is deposited in a pure form as a yellow oil, and the yield is extremely good. In actual practice, it is not necessary to use sufficient water to dissolve the whole of the sodium hydrogen sulphite compound. The nitrile is easily converted into the acid by treating it with thrice its volume of concentrated hydrochloric acid, much heat being developed by the action. J. J. S.

Condensation of Mandelic Acid with Phenols. II. By AUGUSTIN BISTRZYCKI and J. FLATAU (*Ber.*, 1897, **30**, 124—131. Compare Abstr., 1895, i, 419). When crude orthohydroxydiphenylacetic lactone is washed with sodium carbonate solution and the liquid acidified, *parahydroxydiphenylacetic acid*, $OH\cdot C_6H_4\cdot CHPh\cdot COOH$, is precipitated; when pure, this crystallises in concentric groups of flat needles, melting at 173°, and is a comparatively strong acid. The basic barium salt, $BaC_{14}H_{10}O_3 + 4H_2O$, separates in nodular crystals, which lose $3H_2O$ at 125°.

Orthobenzoxydiphenylacetic acid, $OBz\cdot C_6H_4\cdot CHPh\cdot COOH$, crystallises in groups of tablets, and melts at 152.° *Orthohydroxydiphenylbromacetic lactone*, $CPhBr<\begin{matrix}C_6H_4\\CO\ -\end{matrix}>O$, is formed by the action of bromine on the lactone in benzene solution; it crystallises in small tablets, and melts at 70°; when boiled with alcohol, the bromine atom is removed and *ethoxyorthohydroxydiphenylacetic lactone* is formed; this crystallises in small prisms melting at 85—86°. It is sparingly soluble in sodium carbonate, readily in aqueous potash, yielding a solution from which acids precipitate *ethoxyorthohydroxydiphenylacetic acid*,

$$OH\cdot C_6H_4\cdot CPh(OEt)\cdot COOH;$$

this crystallises in microscopic needles, and melts and decomposes at 131°.

Mandelic acid does not appear to undergo condensation with nitrophenols or phenolic ethers, but reacts with many of the homologues of phenol.

Basic barium phenylparahydroxytolylacetate, $C_{15}H_{12}O_3Ba + 4H_2O$, resembles the corresponding diphenyl compound.

Phenylparahydroxytolylbromacetic lactone,

$$CO{<}{}^{CPhBr}_{\;\;\;\;\;O}{>}C_6H_3Me\ [Me:C:O = 1:3:4],$$

melts at 94—96°. *Phenylmetahydroxytolylacetic lactone* [Me : C : O = 1 : 2 : 3 or 1 : 4 : 3] crystallises in needles melting at 122°, and has not hitherto been converted into the corresponding acid.

Phenylquinylacetic lactone,

$$CO{<}{}^{CPhH}_{\;\;\;\;\;O}{>}C_6H_3{\cdot}OH\ [C:O:OH = 1:2:5],$$

crystallises in nodular aggregates melting at 153—154°.

Phenyl-β-hydroxynaphthylacetic lactone forms slender prisms, melting at 184°. A. H.

Elimination of Sulphur from Resorcinoldithiocarboxylic Acid. By Carl Schall (*J. pr. Chem.*, 1896, [2], **54**, 415—421).—Resorcinoldithiocarboxylic acid is entirely freed from sulphur on treatment with alcoholic potash and excess of methylic iodide, although if the latter is not added it remains unchanged. On reduction with sodium amalgam and acidifying, a yellowish-white precipitate is produced, which yields an acetyl compound, evidently *tetracetoxydibenzyl*,

$$C_2H_4[C_6H_3(OAc)_2]_2\ [(OAc)_4 = 2:4:2':4'],$$

melting at 105—112°; from the filtrate, excess of bromine precipitates a red-brown powder, which on acetylation and recrystallisation from glacial acetic acid melts at 215—220°; it is probably *dibromotetracetoxydibenzyl*, $C_2H_4[C_6H_2Br(OAc)_2]_2$. On reducing it in acid solution (zinc and acetic acid), cresorcinol melting at 100—104° is obtained. It is, therefore, possible by this means to introduce a methyl group into the resorcinol nucleus.

Di-α-hydroxynaphthylthione bisulphide,

$$S_2(CS{\cdot}C_{10}H_6{\cdot}OH)_2\ [OH : CSS : 1 : 2],$$

is obtained by heating α-naphthol with potassium sulphide and carbon bisulphide for 12 hours on the water bath. It is a red powder which on acetylation gives a methylation product soluble in alkalis. J. F. T.

Action of Sulphur on Unsaturated Organic Compounds. Bisulphide of Thiobenzoylthiacetic Acid. By Eugen Baumann and Emil Fromm (*Ber.*, 1897, **30**, 110—117).—The *bisulphide of thiobenzoylthioacetate* $S{<}{}^{S-CPh}_{CO\cdot CH}$, is formed when ethylic cinnamate is heated with sulphur; it crystallises in yellowish, almost odourless tablets, melts at 117°, and when distilled with aqueous potash, it yields acetophenone, a proof that one of the sulphur atoms is united with the carbon atom which is directly combined with the

benzene nucleus. Phenylhydrazine converts the bisulphide into bisdiphenylpyrazolone, $C_{30}H_{22}N_4O_2$. The bisulphide is accompanied by small amounts of thioacetophenone, ethylic phenylpropionate and diphenylthiophen. A. H.

Condensation of Ethereal Salts of γ-Disubstituted Itaconic Acids with Aldehydes and Ketones. By HANS STOBBE (*Ber.*, 1897, **30**, 94—97).—*Ethylic diphenylitaconate* was prepared by passing gaseous hydrogen chloride into a boiling alcoholic solution of the acid; it melts at 44—45°. When it is mixed with benzaldehyde and the mixture added gradually to alcoholic sodium ethoxide cooled to −18°, the sodium salt of *γ-diphenyl-α-benzylideneitaconic acid*,

$COOH \cdot C(CHPh) \cdot C(CPh_2) \cdot COOH$,

separates; this acid turns red when heated, and then melts at 207°; its *calcium salt* crystallises with $3H_2O$ and is very sparingly soluble in water.

Ethylic methylphenylitaconate boils at 305—307°; by condensation with benzil in the presence of sodium ethoxide it yields yellow *α-desylene-γ-phenylmethylitaconic acid*,

$COOH \cdot C(CPh \cdot CPhO) \cdot C(CMePh) \cdot COOH$,

melting at 227—230°, the *potassium* salt of which is white, anhydrous, and sparingly soluble. If a freshly-prepared ethereal solution of the acid is treated with piperidine, a piperidine salt, melting and decomposing at 100°, separates; if the ethereal solution has first been allowed to remain for a few days in the light, the piperidine salt which separates melts and decomposes at 200°; the original acid is regenerated from both of these salts, which are probably stereoisomeric.

γ-Phenylmethyl-α-isopropyleneitaconic acid,

$COOH \cdot C(:CMe_2) \cdot C(:CMePh) \cdot COOH$,

was obtained from ethylic phenylmethylitaconate and acetone; it melts and decomposes at 223°. C. F. B.

Action of Phenyl Iodosochloride on Mercury Diphenyl: Production of Phenyl Iodochloride and other Compounds.—By H. CONRAD C. WILLGERODT (*Ber.*, 1897, **30**, 56—58. Compare Abstr., 1895, i, 635.)—When mercury diphenyl and phenyl iodosochloride are agitated during 15 minutes with water, and finally heated until the water boils, diphenyliodinium chloride and phenylmercurichloride are formed, and the same products are obtained if the original compounds are agitated with water at the ordinary temperature during 4 hours. M. O. F.

Thiobenzophenone. By LUDWIG GATTERMANN and H. SCHULZE. (*Ber.*, 1897, **29**, 2944—2945).—It is not possible to obtain absolutely pure thiobenzophenone by the method previously described, namely, the action of phosphorus pentasulphide on benzophenone in benzene solution. A very pure product is, however, obtained if benzophenonechloride be treated with an alcoholic solution of potassium sulphide, prepared by saturating an alcoholic solution of potassium hydroxide with hydrogen sulphide. The thiobenzophenone thus obtained distils at 174° (14 mm.) as a fine, deep blue oil, which soon solidifies to long, blue needles. A sharp melting point cannot be observed, but the thioketone melts lower than benzophenone. With alcoholic potas-

sium hydroxide, it is reconverted into benzophenone; with hydroxylamine, it gives benzophenoxime, and, on heating with copper oxide, it yields tetraphenylethylene. J. F. T.

Derivatives of Benzophenone. By PIETRO BARTOLOTTI (*Gazzetta*, 1896, **26**, ii, 433—441).—*Benzoylguaiacol* is formed with development of heat on adding benzoic chloride to a solution of guaiacol in soda; it forms white crystals, melting at 52—53°. When heated on the water bath with benzoic chloride and anhydrous zinc chloride, hydrogen chloride is evolved, and on treating the mass with water and sodium carbonate, a residue is obtained which yields lustrous, colourless crystals of *benzoylbenzoguaiacol*, $OMe\cdot C_6H_3Bz\cdot OBz$, melting at 95—96·5° after crystallisation, first from alcohol and subsequently from ethylic acetate and petroleum. On warming its alcoholic solution with alcoholic soda, and acidifying with sulphuric acid, *benzoguaiacol*, $OMe\cdot C_6H_3Bz\cdot OH$ [$OMe : OH = 1 : 2$], is obtained; it separates from alcohol in large, pale yellow crystals melting at 131—132°, and is constitutionally related to cotoïn and hydrocotoïn.

On warming a mixture of trimethylpyrogallol, benzoic chloride, and anhydrous zinc chloride on the water bath, hydrogen chloride is evolved, and after treating with water and sodium carbonate, and crystallising from dilute acetic acid, large yellow crystals of *benzopyrogallol dimethylic ether*, $C_6H_2Bz(OMe)_2\cdot OH$, [$(OMe)_2 : OH = 1 : 2 : 3$], melting at 130—131°, are obtained. It is isomeric with hydrocotoïn in which $(OMe)_2 : OH = 1 : 3 : 5$, and is accompanied by small quantities of *benzoylpyrogallol dimethylic ether*, $C_6H_3(OMe)_2\cdot OBz$, which crystallises in large, colourless prisms melting at 116—117°.

On determining the methoxyl present in benzoguaiacol and in benzopyrogallol dimethylic ether, by treating with hydriodic acid by Zeisel's method, two substances are obtained which are still under examination; they are probably the corresponding ketophenols.

W. J. P.

α-Amido-β-naphthylic Ethylic Ether. By LUDWIG PAUL (*Zeit. angw. Chem.*, 1896, 620—622).—Instructions are given for the manufacture of the ethylic ether of α-amido-β-naphthol. β-naphthol is first etherified, and the ether is then mixed with its own weight of water and treated with the requisite quantity of nitric acid (40°Bé.); the α-nitro-compound obtained in this way yields the α-amido-β-naphthylic ethylic ether on reduction with zinc dust and hydrochloric acid. On treating the amido-ether with acetic anhydride in benzene solution, it is converted into a *monacetyl derivative*, which crystallises in slender, colourless needles, and melts at 144°.

β-Naphthylic methylic ether, when nitrated, yields an α-nitro-derivative, which crystallises from alcohol in large, colourless plates, melts at 125·5°, and on reduction yields the corresponding amido-compound. These ethers of α-amido-β-naphthol can be used in the manufacture of dyes in place of α-naphthylamine. J. J. S.

Naphthacetol. By OTTO N. WITT and JENS DEDICHEN (*Ber.*, 1897, **29**, 2945—2954).—It is well known that the value of the azo-dyes derived from β-naphthol lies in the fact that the combination with

the diazo-chloride takes place in the ortho-position relatively to the hydroxyl group, and that the compound thus formed retains only to a very slight extent the phenolic character of the parent substance. In α-naphthol, on the other hand, of the positions 2 and 4 in which the diazo-group can enter, preference is nearly always given to the position 4, and the dye formed is, therefore, strongly phenolic and basic in character, a fact which considerably affects its dyeing properties.

If, however, the diazo-group be made to combine in the ortho-position relatively to the hydroxyl, the dyes are then quite as fast to light as those derived from β-naphthol, and even surpass them in shade. This combination can be brought about by the presence of an inert group in the para-position in α-naphthol.

4-Acetamido-α-naphthol (parahydroxy-α-acetonaphthalide),

$$C_8H_6(OH)\cdot NHAc\ [=1:4],$$

for which the name *naphthacetol* is proposed, is a substance which fulfils these conditions. It is best prepared by the method of Grandmougin and Michel by the acetylation of paramido-α-naphthol with acetic anhydride; it forms slender, white needles melting at 187° after recrystallisation from alcohol. Naphthacetol readily reacts with most diazo-compounds with the production of azo-compounds analogous to those derived from β-naphthol, but somewhat bluer in shade.

Benzeneazonaphthacetol is formed when an alcoholic solution of naphthacetol is treated with diazobenzene chloride; when recrystallised from pyridine, it forms red needles melting at 267—268°. On dissolving the dye in an alcoholic solution of potash, and adding the requisite quantity of methylic iodide, the *methylic ether* is obtained, a scarlet-red, crystalline substance melting at 218—220° after recrystallisation from xylene. The production of this methylic ether shows that the phenolic character of the hydroxyl-group is not quite destroyed.

Naphthacetol combines with diazosulphonic acids with the production of soluble dyes very similar to those derived from β-naphthol.

It does not appear possible to obtain the amido-derivative of naphthacetol by the reduction of the azo-dye; the compound is certainly formed, but decomposes on attempts being made to recrystallise it. It is readily converted into the corresponding *quinone* on treating its aqueous solution with excess of ferric chloride; the quinone separates from dilute alcohol in orange-red needles melting and decomposing at 220°. If the diazo-group has in reality entered in the ortho-position relatively to the hydroxyl-group, this compound must be a derivative of β-naphthaquinone; this was proved to be the case by the production of an *acetylphenonaphtheurhodine* by combining it with orthophenylenediamine in acetic acid solution. This compound crystallises from phenol or alcohol in lemon-yellow needles which do not melt at 360°; on treatment with concentrated hydrochloric acid, it yields blood-red needles of the hydrochloride of phenonaphtheurhodine, which can be converted into the eurhodine by treatment with ammonia. This eurhodine melts at 294°, and is in every respect identical with typical eurhodine. The production of hydroxynaphthaquinone and of acetyleurhodine, moreover, shows that the diazo-group has entered in the ortho-position relatively to the hydroxyl.

Naphthacetol, like β-naphthol, readily yields a *nitroso*-derivative, which crystallises from glacial acetic acid in golden needles melting at 203°.

By employing other acid anhydrides in the acidylation of paramido-α-naphthol, homologues of naphthacetol are produced. 4-*Butyramido-α-naphthol* crystallises from alcohol in colourless, flat needles melting at 160—161°. 4-*Valeramido-α-naphthol* forms colourless crystals melting at 204—205°. 4-*Benzamido-α-naphthol* separates from alcohol in glistening, white needles melting at 228—229°. This benzoyl derivative can also be prepared by the Baumann-Schotten method from the hydrochloride of amidonaphthol and benzoic chloride.

J. F. T.

1:1′-Dihydroxynaphthalene-4-sulphonic Acid. By LUDWIG PAUL (*Zeit. angw. Chem.*, 1896, 619—620).—To prepare 1:1′-dihydroxynaphthalene-4-sulphonic acid, α-naphthol-δ-disulphonic acid is fused with sodium hydroxide at 210—215° for some 2½ hours. Details are given for the manufacture of the acid on the large scale. J. J. S.

Colouring Matters Derived from the Sulphonic Acids of α-Naphthol and α-Naphthylamine. By LUDWIG GATTERMANN and H. SCHULZE (*Ber.*, 1897, **30**, 50—55).—The two following laws have been established with regard to the production of azo-colouring matters from the sulphonic acids of α-naphthol and α-naphthylamine: 1. When the para-position with respect to the hydroxy- or amido-group is free, and the neighbouring positions in either benzene nucleus are not substituted by a sulphonic group, colouring matters of the para-series are obtained. 2. When substitution has occurred in the para-position, or the sulphonic radicle occupies either of the neighbouring positions, colouring matters of the ortho-series are formed, provided substitution in this position has not previously occurred.

The colouring matters obtained by the action of diazo-compounds on 1 : 4′-hydroxynaphthalenesulphonic, 1 : 4′-amidonaphthalenesulphonic, 1 : 3-hydroxynaphthalenesulphonic, 1 : 3-amidonaphthalenesulphonic, and 1 : 2 : 4′-hydroxynaphthalenedisulphonic acids have been studied from this point of view.

1 : 4′-Hydroxynaphthalenesulphonic acid, when dissolved in soda and treated with diazobenzene chloride, yields the *sodium* salt of 2-benzeneazo-1 : 4′-hydroxynaphthalenesulphonic acid, which crystallises from water in red leaflets; this colouring matter is known as cochineal scarlet G. Reduction with stannous chloride and hydrochloric acid gives rise to 2 : 1 : 4′-amidohydroxynaphthalenesulphonic acid, and this substance, on treatment with sodium amalgam, yields 2 : 1-amidohydroxynaphthalene, and not the 1 : 4-derivative.

1 : 4′-Amidonaphthalenesulphonic acid combines with diazobenzene, forming 2-benzeneazo-1 : 4′-amidonaphthalenesulphonic acid, the *sodium* salt crystallising from water in beautiful red leaflets; the *benzylidene* derivative is a white, crystalline substance, which resists the action of hydrochloric acid at 150°. Reduction with stannous chloride and hydrochloric acid gives rise to 1 : 2 : 4′-diamidonaphthalenesulphonic acid, which, on treatment with sodium amalgam, is converted into 1 : 2-naphthylenediamine.

The *sodium* salt of 2-benzeneazo-1 : 3-naphthalenesulphonic acid is obtained from 1 : 3-naphthalenesulphonic acid and diazobenzene chloride, and crystallises from water in red leaflets resembling eosin; when reduced with stannous chloride, it yields 2 : 1 : 3-amidohydroxynaphthalenesulphonic acid, and this is converted into 2 : 1-amidohydroxynaphthalene under the influence of sodium amalgam.

1 : 3-Amidonaphthalenesulphonic acid does not combine with diazobenzene chloride, but the action of paranitrodiazobenzene chloride gives rise to a reddish-violet colouring matter, which yields 1 : 2 : 3-naphthylenediaminesulphonic acid on reduction; when this is reduced with sodium amalgam 1 : 2-naphthylenediamine is formed.

M. O. F.

Hydroxlyamine Derivatives of Anthraquinone. By ROBERT E. SCHMIDT and LUDWIG GATTERMANN (*Ber.*, 1897, **29**, 2934—2943).—In the reduction of nitro-anthraquinones to the corresponding amido-compounds by means of alkaline reducing agents, green to blue intermediate products are obtained, which are soluble in alkalis and are converted by further reduction into the amido-derivatives. These intermediate products are the hydroxylamine derivatives of anthraquinone, and are well defined crystalline substances which, on treatment with concentrated sulphuric acid, undergo intramolecular rearrangement, being converted into the corresponding amidohydroxyanthraquinones.

1 : 4′-*Dihydroxylamineanthraquinone*,

$$OH\cdot NH\cdot C_6H_3<^{CO}_{CO}>C_6H_3\cdot NH\cdot OH\ [=1:4'],$$

is obtained on reducing 1 : 4′-dinitroanthraquinone with stannous chloride and sodium hydroxide, the 1 : 4′-dinitroanthraquinone being the one which yields anthrarufin on reduction, diazotising the diamido-derivative thus formed, and heating the tetrazo-derivative with acids. The substance has no definite melting point, but the pure blue colour of its alkaline solution is characteristic. It dissolves in concentrated hydrochloric acid, forming a colourless solution, which, however, on dilution, yields the hydroxylamine compound again unchanged. By further reduction, it passes into 1 : 4′-diamidoanthraquinone. The *dibenzoyl* derivative, obtained by the action of 2 mols. of benzoic chloride on 1 mol. of the hydroxylamine compound, consists of garnet-red needles melting at 188°. In strong alkaline solutions, and employing an excess of benzoic chloride, the *tribenzoyl* derivative, an orange-yellow compound melting at 228°, can be obtained. On heating 1 : 4′-dihydroxylamineanthraquinone with concentrated sulphuric acid, it readily undergoes molecular rearrangement, with the production chiefly of two isomeric diamidodihydroxyanthraquinones, called respectively the α and β, together with a third, the γ, in somewhat smaller quantities. These can be separated from one another by taking advantage of their relative solubilities in dilute sulphuric acid, alkalis and acetone.

α-Diamidodihydroxyanthraquinone dissolves in hot nitrobenzene, forming a violet-blue solution, which, on cooling, deposits long, brassy needles; it dissolves in concentrated sulphuric acid, and the yellow solution, on the addition of boric acid, becomes blue, and then shows a sharp and characteristic absorption spectra.

β-Diamidodihydroxyanthraquinone crystallises from acetone in dark,

metallic green crystals, which also give a characteristic absorption spectra when treated in the manner described above.

γ-*Diamidodihydroxyanthraquinone*, which is obtained only in small quantities, dissolves in sulphuric acid, forming a yellow solution which is not altered by adding boric acid to it. If, however, it is heated with a 10 per cent. solution of boric acid in concentrated sulphuric acid at 80—100°, a fine, bluish-red solution is obtained, having a cinnabar-red fluorescence, and showing a characteristic absorption band in the green.

By the action of sulphur and fuming sulphuric acid at ordinary temperatures on 1 : 4′-dinitroanthraquinone, the chief products are the above-mentioned α-and β-diamidodihydroxyanthraquinones, together with a small quantity of a third substance, which is probably identical with the γ-compound ; at the same time, a fourth substance (δ) containing sulphur is produced.

On nitrating anthrarufin and subsequently reducing the dinitro-derivative, a compound identical with the previously described α-diamidodihydroxyanthraquinone is formed ; this must be a diparamidoanthrarufin of the formula

$$NH_2\cdot C_6H_2(OH)<{}^{CO}_{CO}>C_6H_2(OH)\cdot NH_2,\ [(OH_2):(NH_2)_2 = 1:4':4:1']$$

1 : 4′-*Nitrohydroxylamineanthraquinone*,

$$OH\cdot NH\cdot C_6H_3<{}^{CO}_{CO}>C_6H_3\cdot NO_2,$$

is obtained on reducing 1:4′-dinitroanthraquinone with phenylhydrazine and alcohol ; it crystallises from acetone in long needles.

1 : 1′-*Dihydroxylamineanthraquinone*,

$$OH\cdot NH\cdot C_6H_3<{}^{CO}_{CO}>C_6H_3\cdot NH\cdot OH,$$

is formed from 1 : 1′-dinitroanthraquinone, that is, the dinitroanthraquinone which, on reduction, &c., yields chrysazin ; the reduction is conducted in the same manner as in the case of the 1 : 4′ compound, its solution in alkalis is green.

1:1′-*Nitrohydroxylamineanthraquinone*,

$$OH\cdot NH\cdot C_6H_3<{}^{CO}_{CO}>C_6H_3\cdot NO_2,$$

is insoluble in a solution of sodium hydroxide ; it crystallises from pyridine and methylic alcohol in glistening crystals.

1:-*Hydroxylamineanthraquinone* is formed on reducing 1-nitroanthraquinone with the requisite quantity of stannous chloride and sodium hydroxide in aqueous alcoholic solution. It separates from acetone in fine, red-brown crystals which dissolve in a solution of sodium hydroxide, yielding a green solution. On treatment with concentrated sulphuric acid, it is transformed into an amidohydroxyanthraquinone, which, since it can be produced by the action of sulphur sesquioxide on the mononitroanthraquinone, as well as by the action of ammonia on quinizarin, must have the constitution

$$C_6H_4<{}^{CO}_{CO}>C_6H_2(OH)\cdot NH_2[OH:NH_2:1:4].$$

J. F. T.

Oil of Roses. By Eugène Charabot and G. Chiris (*Compt. rend.*, 1896, **123**, 752—753).—In the examination of a large number of

samples of rose-water, the authors have always observed the presence of a certain amount of acid (about 0·0003 gram per litre as acetic acid). This they regard as confirmatory of the statement made by Dupont and Guerlain (this vol., i, 160), to the effect that oil of roses contains an ether which is hydrolysed by prolonged boiling with water. If the primitive apparatus employed in the distillation of the oil in the East had been used, the authors are of opinion that they would have found larger amounts of acid than in the samples of rose-water with which they worked. A. C. C.

Artificial Production of Pulegone from Citronellaldehyde. By FERDINAND TIEMANN and R. SCHMIDT (*Ber.*, 1897, **30**, 22—32). —In view of the fact that pulegone yields acetone and methylcyclohexenone when heated with formic acid (Abstr., 1896, i, 309), the behaviour of isopulegone, obtained from isopulegol (Abstr., 1896, i, 383), towards this agent has been studied. Isopulegol is the alcohol obtained in the form of acetate when citronellaldehyde is heated with an equal weight of acetic anhydride under pressure, and on treating the corresponding ketone with formic acid, methylcyclohexenone is obtained, identical in every respect with the substance produced from pulegone; the identity, however, does not extend to the original ketones and alcohols, which exhibit certain differences among themselves. For instance, natural pulegone boils at 99—101° under a pressure of 12 mm., and forms a crystalline sodium hydrogen sulphite compound, whilst isopulegone boils at 90° under a pressure of 12 mm., and does not combine with sodium hydrogen sulphite; pulegol obtained from natural pulegone, and containing a small quantity of menthol, boils at 108—110° under a pressure of 14 mm., whilst isopulegol boils at 91° under a pressure of 13 mm. Moreover, natural pulegone and pulegol readily yield menthol when reduced with sodium and alcohol, whilst alcoholic solutions of isopulegone and isopulegol resist the action of the metal. Another difference between pulegone and isopulegone lies in their behaviour towards hydroxylamine, the former yielding a normal oxime, $C_{10}H_{17}NO$, which melts at 118—119°, and an oxime, $C_{10}H_{19}NO_2$, which melts at 147° (compare Beckmann and Pleissner, Abstr., 1891, 936); isopulegone forms two oximes, which have the same composition,

$$C_{10}H_{17}NO,$$

but melt at 120—121° and 134° respectively. Again, the semicarbazones of pulegone and isopulegone melt at 172° and 173° respectively, but they are not identical, as the crystals which separate from the mixed alcoholic solutions melt at a temperature considerably lower.

Isopulegone (Abstr., 1896, i, 383) in a 1 decimetre tube has $\alpha_D = +10° 15'$; the sp. gr. = 0·9213 at 17·5°, the refractive index $n_D = 1·4690$, and the molecular refraction M = 45·98. As already stated, it does not yield a compound with sodium hydrogen sulphite, and when treated with sodium and alcohol, is converted into isopulegol, no menthol being produced. When the ketone is agitated during 50—60 hours with 5 per cent barium hydroxide, however, it is completely converted into pulegone, which is also formed when isopulegone is allowed to remain in alcoholic solution with 5 per cent. barium hydroxide at ordinary temperatures.

The authors suggest the possibility of representing isopulegol by

the formula $\begin{matrix}CHMe-CH_2\\ |\\ CH_2\cdot CH(OH)\end{matrix}\!\!>\!CH\cdot CH\colon CMe_2$ ascribing to isopulegone the formula $\begin{matrix}CHMe\cdot CH_2\\ |\\ CH_2 —— CO\end{matrix}\!\!>\!CH\cdot CH\colon CMe_2$; this explanation of the isomerism however, involves the conversion of the last-named substance into pulegone, $CHMe\!<\!\begin{matrix}CH_2—CO\\ CH_2\cdot CH_2\end{matrix}\!>\!C\colon CMe_2$, under the influence of barium hydroxide. M. O. F.

Dextro and Lævo Configurations in the Citronellal Series. By Ferdinand Tiemann and R. Schmidt (*Ber.*, 1896, **30**, 33—38).—It has been shown that, whilst citronellaldehyde, citronellol, citronellic acid, and the β-methyladipic acid, to which they give rise on oxidation, are dextro-rotatory, rhodinol, from Turkish rose oil, constitutes the citronellol of the lævo-gyrate series; other members of both groups have now been obtained.

The *semicarbazone* of *d*-citronellaldehyde crystallises in leaflets, and melts at 82·5°. The nitrile of *d*-citronellic acid boils at 104—106° under a pressure of 14 mm. (compare Semmler, Abstr., 1893, i, 685).

By the oxidation of *l*-citronellol (from rose oil), a small quantity of *l*-citronellaldehyde has been obtained, along with *l-citronellic acid*, which boils at 143—144°, under a pressure of 14 mm., has, in a 1 decimetre tube, $a_D = -6° 15'$, and the refractive index $n_D = 1·4536$ at 20°; the *silver* salt is unstable, and does not dissolve in water. Citronellic acid, obtained from Reunion geranium oil, is a mixture of *d*- and *l*-citronellic acids.

Menthone is not produced when Reunion geranium oil (pelargonium oil) is oxidised, as stated by Barbier and Bouveault; the ketone obtained from this source is isopulegone. M. O. F.

Camphor. By J. C. W. Ferdinand Tiemann (*Ber.*, 1897, **30**, 242—265. Compare Abstr., 1895, i, 426 and 675; also this vol., i, 161).—β-Campholenonitrile, $CN\cdot CH_2\cdot CH\!<\!\begin{matrix}CH=CH\\ CMe_2\cdot CHMe_2\end{matrix}$, is obtained when the dehydration of camphoroxime is effected by the agency of concentrated acids, isoamidocamphor, β-campholenamide, and dihydrocampholenolactone being also produced; it is optically inactive, boils at 225°, and has the odour of the α-modification. Reduction in alcoholic solution with sodium gives rise to β-camphylamine, which is optically inactive, and boils at 196—198°.

β-Campholenamide, $NH_2\cdot CO\cdot CH_2\cdot CH\!<\!\begin{matrix}CH=CH\\ CMe_2\cdot CHMe\end{matrix}$, is produced on hydrolysing the β-nitrile with alcoholic potash, and is also formed when ammonium β-campholenate is heated in sealed tubes at temperatures above 200° during several hours; an aqueous solution of isoamidocamphor hydrochloride also yields β-campholenamide when boiled; it crystallises in long, colourless needles, melts at 86°, and is optically inactive.

β-Campholenic acid, $COOH\cdot CH_2\cdot CH\!<\!\begin{matrix}CH=CH\\ CMe_2\cdot CHMe\end{matrix}$, is obtained by hydrolysing the nitrile, or amide, with alcoholic potash, and melts at

52°, boiling under atmospheric pressure at 245°; the *ammonium* salt crystallises in small prisms and melts at 130°; the *calcium* salt forms slender needles, and the *ethylic* salt is a colourless, optically inactive oil which boils at 222—225° under atmospheric pressure.

β-Dihydroxydihydrocampholenic acid,

$$COOH\cdot CH_2\cdot CH<\begin{matrix}CH(OH)\cdot CH\cdot OH\\ CMe_2 \text{---} CHMe\end{matrix},$$

is formed when β-campholenic acid is oxidised with potassium permanganate; it crystallises from chloroform or water in slender, lustrous needles, and melts at 146°. The acid sublimes under atmospheric pressure without undergoing decomposition, whilst the α-modification yields water and *l*-pinonic acid. 3 : 4 : 4-*Trimethylheptan-2-oldioic acid*, $COOH\cdot CH_2\cdot CH_2\cdot CMe_2\cdot CHMe\cdot CH(OH)\cdot COOH$, is also a product of the action of potassium permanganate on β-campholenic acid; the substance is an unstable syrup, and when distilled under atmospheric pressure, or in a current of steam, it yields an unsaturated cyclic ketone, isocamphorone, having the composition $C_9H_{14}O$.

Isocamphorone, $CO<\begin{matrix}CH_2\cdot CH_2\\ CH:CMe\end{matrix}>CMe_2$, is obtained by concentrating the liquid produced on oxidising β-campholenic acid with potassium permanganate, acidifying with sulphuric acid, and distilling the product in an atmosphere of steam; it boils at 97—99° under a pressure of 13 mm., and at 217° under atmospheric pressure. The ketone has the odour of camphorone, with which it is isomeric; the sp. gr. = 0·9424 at 20°, and the refractive index $n_D = 1{\cdot}48458$, whence the molecular refraction, M = 41·93. The *semicarbazone* crystallises from ethylic acetate in long needles, and melts at 211°. *Hydroxylamidodihydrocamphorone oxime*, $NOH:C<\begin{matrix}CH_2 \text{------------} CH_2\\ CH(NH\cdot OH)\cdot CHMe\end{matrix}>CMe_2$, is obtained by the action of alcoholic hydroxylamine on the ketone, being produced when the latter is present in excess; it separates in large, lustrous crystals and melts at 153°. Fehling's solution is at once reduced by an alcoholic solution of the substance.

Campholonic acid, $COOH\cdot CH_2\cdot CH<\begin{matrix}CO\text{---}CH_2\\ CMe_2\cdot CHMe\end{matrix}$, remains in the acid liquid after removing isocamphorone by means of a current of steam; it has not been hitherto obtained in crystalline form, but the *sodium* salt crystallises readily, and the *semicarbazone* melts at 224°. Campholonic acid is isomeric with the pinonic acids, but, on treatment with sulphuric acid, yields a ketone which is probably dihydroisocamphorone; the pinonic acids give rise to methoethylheptanonolide.

3-*Dimethylhexan-2-onoic acid* (acetyldimethylbutyric acid),

$$COMe\cdot CMe_2\cdot CH_2\cdot CH_2\cdot COOH,$$

is produced on oxidising β-dihydroxydihydrocampholenic acid with chromic acid (Abstr., 1895, i, 677), and crystallises from water in lustrous prisms; it melts at 48°, and boils at 150°, 160·5°, and 178° under pressures of 10 mm., 13 mm., and 20 mm. respectively. The *ammonium* salt melts at 110°, and the *semicarbazone* at 185°; the acid is also formed when isocamphorone is oxidised with potassium permanganate. When the oxidation of β-dihydroxydihydrocampholenic acid is effected

with a considerable quantity of chromic acid, asymmetric α-dimethylglutaric acid (m. p. 85°) is produced; dimethylglutaric acid is also obtained on oxidising isocamphorone.

Although mineral acids convert β-campholenic acid into dihydrocampholenolactone, nitric acid oxidises a portion of the substance before the lactone is produced (compare Abstr., 1896, i, 55); volatile, fatty acids, asymmetric α-dimethylglutaric and dimethylsuccinic acids are obtained in this way, along with isocamphoronic acid.

A discussion of the constitution of β-campholenic derivatives, and their products of change, follows the experimental details.

M. O. F.

Action of Aluminium Chloride on Camphoric Anhydride. By G. Blanc (*Compt. rend.*, 1896, **123**, 749—752).—In investigating the action of aluminium chloride on camphoric anhydride dissolved in benzene, Bürcker obtained a condensation product of the two substances with disengagement of carbonic oxide (Abstr., 1896, i, 179). The author has studied the action of aluminium chloride on the anhydride in the presence of an inert solvent—chloroform. The product of the action, which was attended with evolution of carbonic oxide and hydrogen chloride, was an acid of the formula $C_9H_{14}O_2$. From dilute alcohol, it separates in colourless crystals melting at 132—133° and boiling at 247—249°; it dissolves readily in all the ordinary organic solvents. The salts of sodium, potassium, calcium, and barium are soluble in water, those of lead, zinc, copper, and cobalt are insoluble in water, but readily soluble in ether. The following ethereal salts were prepared by Meyer's method. All are liquids. *Methylic* salt, boiling at 203—204°. *Ethylic* salt, boiling at 214°. *Normal propylic* salt, boiling at 233—235°. *Isobutylic* salt, boiling at 241—243°. They are easily hydrolysed by alcoholic potash and by concentrated sulphuric acid. By treating the acid with phosphorus pentachloride and fractionating under reduced pressure, the *acid chloride*, $C_9H_{13}OCl$, was obtained as a mobile liquid boiling at 100—102° (40 mm.), and with decomposition at 212—214° under 760 mm. pressure. Ammonia, aniline, and phenylhydrazine react with this substance in ethereal solution, yielding the amide, anilide, and phenylhydrazide respectively. The *amide*, $C_9H_{13}O{\cdot}NH_2$, consists of fine, monoclinic crystals melting at 129—130°; it is readily soluble in alcohol, but only slightly so in light petroleum. The *anilide*, $C_9H_{13}O{\cdot}NHPh$, melts at 104°. The *phenylhydrazide*, $C_9H_{13}O{\cdot}N_2H_2Ph$, occurs as slender, monoclinic crystals melting at 130°. These three compounds are neither hydrolysed by alcoholic potash nor by sulphuric acid. The author is endeavouring to determine the constitution of the acid $C_9H_{14}O_2$. A. C. C.

Onocerin. By Hermann Thoms (*Ber.*, 1896, **29**, 2985—2991).—The roots of *Ononis spinosa L.* yield the glucoside ononin and a substance to which Hlasiwetz has given the name onocerin (*J. pr. Chem.*, 1855, **65**, 419); the latter compound has now been investigated by the author, who regards it as a dihydric secondary alcohol of the composition $C_{26}H_{44}O_2$.

Onocol (onocerin) is obtained by extracting the roots with 90 per cent. alcohol, and treating with 60 per cent. alcohol the residue obtained

on evaporating the extract; onocerin remains undissolved, and is recrystallised from absolute alcohol, from which it separates in colourless, microscopic prisms. The substance dissolves with difficulty in ethylic acetate, ether, and chloroform; it melts at 232°. The *diacetyl* derivative is crystalline, and melts at 224°; the *dibenzoyl* derivative melts at 175—190°. On adding bromine to a solution of the diacetyl derivative in glacial acetic acid, the *tetrabromide* is produced; it melts and decomposes at 140—145°.

Onoketone, $C_{26}H_{40}O_2$, is obtained by dissolving onocerin in glacial acetic acid and adding powdered potassium dichromate to the solution at 60°; it crystallises from alcohol in colourless needles, and melts at 186—187°. The *oxime* is a white, amorphous substance, and the *phenylhydrazone* is also amorphous; the *semicarbazone* melts and decomposes at 175°.

Oxidation of onoketone with chromic acid in glacial acetic acid gives rise to the *acid*, $C_{20}H_{30}O_5$, which melts at 75—80°, and appears to be related to abietic or pimaric acids; acetic and butyric acids appear to be produced when aqueous chromic acid is used.

The similarity between onocol and cholesterol leads the author to regard the former alcohol as belonging to the same class (compare Abstr., 1896, i, 425). M. O. F.

Filicic Acid. By GIROLAMO DACCOMO (*Gazzetta*, 1896, **26**, ii, 441—451).—On boiling a benzene solution of filicic acid with alcoholic hydroxylamine hydrochloride and calcium carbonate for several hours, filtering, distilling off the solvent, and treating with alkali, a residue is obtained which crystallises from alcohol in microscopic, reddish prisms melting at 150° with previous discoloration; it is soluble in alcohol or ether, has an odour of pyridine, and is the *anhydride* of the oxime of filicic acid, $C_{14}H_{15}O_4N$. The alkaline mother liquor obtained during its preparation gives a reddish precipitate with hydrochloric acid, but no pure product could be isolated from it.

By substituting ethylic acetate for benzene in the previous preparation, an *isomeride* of the above anhydride is obtained in microscopic, yellow prisms which melt at 197—198° with previous discoloration.

Copper filicate (Abstr., 1895, i, 68) is slowly converted into cuprous oxide by baryta water, and the liquor on distillation yields acetone, isobutyric acid, butyric acid, dimethylmalonic acid, and carbonic anhydride. This behaviour indicates that filicic acid is an aliphatic ketaldehyde containing the group $CMe_2{\cdot}C{<}^{C}_{C}$. W. J. P.

The Chemistry of Chlorophyll. By LEO MARCHLEWSKI (*J. pr. Chem.*, 1896, [2], **54**, 422—428.)—A reply to Tschirch (Abstr., 1896, i, 624). J. F. T.

Hyposantonous Acid and its Decomposition Products. By GIUSEPPE GRASSI-CRISTĀLDI (*Gazzetta*, 1896, **26**, ii, 451—465).—The same hyposantonous acid is obtained by reducing either hyposantonin or isohyposantonin with zinc dust in acetic acid solution; it has the specific rotation $[\alpha]_D = +75{\cdot}95°$ (compare Andreocci, Abstr., 1896, i, 182). The *barium* salt crystallises with $2H_2O$, and the *silver* salt is a white powder; the *methylic* salt, $C_{15}H_{19}O_2Me$, crystallises in lustrous

prisms melting at 43°, and has the specific rotation $[\alpha]_D = +79.14°$ at 28° in a 6 per cent. methylic alcohol solution.

On heating hyposantonous acid under reduced pressure at 350° with aqueous potash, propionic acid is formed, hydrogen is evolved, and an oil consisting of a mixture of dimethyldihydronaphthalene and 1 : 4-dimethylnaphthalene distils; the mixture is converted into pure 1 : 4-dimethylnaphthalene by heating with iodine. The hydrocarbon thus obtained is identical with that prepared by Cannizzaro and Andreocci (Abstr., 1896, i, 488); its formation from hyposantonous acid confirms Cannizzaro's view respecting the formation of 1 : 4-dimethylnaphthol, and is not in accordance with Klein's opinion (Abstr., 1894, i, 51) respecting the decomposition of santonous acid. W. J. P.

Coal-tar Bases. By FELIX B. AHRENS (*Ber.*, 1896, **29**, 2996—2999. Compare Abstr., 1895, i, 390).—3 : 4-*Dimethylpyridine* (lutidine) has been isolated from the fraction of coal-tar light oil (*loc. cit.*) boiling at 164—165°, which is treated in acidic solution with mercuric chloride (3 mols.); it boils at 163·5—164·5°, and the odour is not disagreeable.

The *hydrochloride*, *hydrobromide*, and *hydriodide* crystallise in needles, and the *platinochloride*, which contains $2H_2O$, melts and decomposes at 205°; the *mercurichloride* crystallises in slender needles, and the *aurochloride* and *picrate* melt at 160—162° and 163° respectively. On oxidising the base with neutral potassium permanganate, 3 : 4-pyridinedicarboxylic (cinchomeronic) acid is produced.

2 : 4 : 5-*Trimethylpyridine* (collidine) is obtained in the form of an oily mercurichloride in isolating the foregoing base, and is purified by conversion into the picrate; it has a spice-like odour, and boils at 165—168°. The *platinochloride* contains $2H_2O$, which is eliminated at 100°, and melts at 205°, and effervesces vigorously; the *mercurichloride*, *aurochloride*, and *picrate* melt at 164—175°, 129—131°, and 128—131°, respectively. Oxidation with potassium permanganate converts the base into 2 : 4 : 5-pyridinetricarboxylic (berberonic) acid.

M. O. F.

Decomposition of Pipecolinic Acid into its two Optical Components. By FRITZ MENDE (*Ber.*, 1896, **29**, 2887—2889).—2-Methylpyridine was oxidised with potassium permanganate, and the 2-carboxylic acid formed was reduced, in boiling alcoholic solution, with sodium. The hot alcoholic solution of the pipecolinic acid thus obtained was heated with just more than enough *d*-tartaric acid to form a hydrogen tartrate with half of it. The *d-hydrogen tartrate* of *d-pipecolinic acid* separated from the cooled solution. This melts at 187°, and, after successive treatment with lead acetate and hydrogen sulphide, yields *d-pipecolinic acid*, which has, in a tube 100 mm. long and at 25°, a rotation varying from +3·63° in a solution of 9·92 per cent. concentration to +7·006° in one of 19·93 per cent.

When the mother liquor from the above-mentioned tartrate was treated successively with lead acetate and hydrogen sulphide, and *l*-tartaric acid added, the *l-hydrogen tartrate* of *l-pipecolinic acid* separated. This exactly resembles the isomeric compound, and, in like manner, the *l-pipecolinic acid* prepared from it resembles *d*-pipecolinic

acid, except that its rotation is to the left ($-3{\cdot}54°$ in a solution of 9·92 per cent. concentration). C. F. B.

Action of Sulphur Bromide on Aromatic Amines. By ALBERT EDINGER (*J. pr. Chem.*, 1896, [2], **54**, 355—358).—The main facts in this paper have already appeared. (Compare this vol., i, 103). J. F. T.

Action of Sulphur Chloride on Quinoline. By ALBERT EDINGER and HANS LUBBERGER (*J. pr. Chem.*, 1896, [2], **54**, 340—358).—The main facts in this paper have already appeared. (Compare this vol., i, 103). J. F. T.

1-Hydroxyquinoline-4-sulphonic Acid and its Derivatives. By ADOLPH CLAUS and ROBERT GIWARTOVSKY (*J. pr. Chem.*, 1896, [2], **54**, 377—391).—1-Hydroxyquinoline-4-sulphonic acid, when brominated, gives rise to 2-*bromo*-1-*hydroxyquinoline*-4-*sulphonic acid* only, the position of the bromine atom being ascertained by its oxidation to quinolinic acid melting at 180°, and the formation from this of nicotinic acid melting at 228°, and also from its yielding 4-bromo-1-hydroxyquinoline (m. p. 124°) when boiled with sulphuric acid.

2-*Bromo*-1-*hydroxyquinoline* sublimes in long, colourless needles melting at 138°.

2-Bromo-1-hydroxyquinoline-4-sulphonic acid crystallises with $\frac{1}{2}H_2O$, from boiling water or hydrochloric acid; its salts, both normal and basic, are soluble in water.

The unbrominated hydroxysulphonic acid, after treatment for 24 hours with tin and hydrochloric acid, is completely reduced to tetrahydroquinoline-4-sulphonic acid, and the bromo-compound, when treated in the same way, yields tetrahydro-1-hydroxyquinoline-4-sulphonic acid, which is further reduced to tetrahydroquinoline-4-sulphonic acid, melting at 315°, if the reducing agent is allowed to act twice as long.

2-*Chloro*-1-*hydroxyquinoline*-4-*sulphonic acid* is best obtained by the action of chlorine on a solution of the sulphonic acid in hydrochloric acid, the product being mixed with a small quantity of 2 : 4-*dichloro*-1-*hydroxyquinoline*, which crystallises from alcohol in colourless needles melting at 179°. The pure chlorhydroxyquinolinesulphonic acid crystallises from its aqueous alcoholic solution in colourless needles and prisms containing $1H_2O$. Like the bromo-compound, it yields pyridinedicarboxylic acid and nicotinic acid on oxidation with potassium permanganate, thus proving the position of the chlorine atom. On treatment with sulphuric acid, the sulphonic acid group is eliminated, and 2-*chloro*-1-*hydroxyquinoline*, a compound crystallising in colourless needles and melting at 145°, is produced.

By the action of phosphorus pentachloride on 1-hydroxyquinoline-4-sulphonic acid, the sulphonic acid group is readily replaced by the halogen with the production of Hebebrand's 4-chloro-1-hydroxyquinoline melting at 125°, whilst phosphorus pentabromide gives rise to 2 : 4 : 3′-tribromo-1-hydroxyquinoline melting at 170°. It was not found possible to obtain the corresponding trichloro-derivative by this means; by prolonging the action of the pentachloride, other products were formed which are still under investigation. J. F. T.

1-Benzoyl-4-phenylthiosemicarbazide. By WILHELM MARCKWALD and AUG. BOTT (*Ber.*, 1896, **29**, 2914—2920).—1-*Benzoyl*-4-*phenylthiosemicarbazide*, NHPh·CS·NH·NHBz, cannot be obtained by the action of benzoic chloride on phenylthiosemicarbazide, but is formed when phenylcarbimide and benzhydrazide are brought together in alcoholic solution. It forms white crystals, and melts at 162°. When treated with acetic chloride, it is converted into diphenylimidothiobiazoline, $NPh:C\!<\!\begin{matrix}S—CPh\\ \quad\ \ \| \\ NH\cdot N\end{matrix}$, which is identical with a product previously obtained by Pulvermacher (Abstr., 1894, i, 304), by the action of benzoic chloride on phenylthiosemicarbazide. It has basic properties, and forms a sparingly soluble *hydrochloride* and *platinochloride*. The *acetyl* derivative melts at 140°. The base also forms a *nitroso*-compound, $C_{14}H_{10}N_4SO$, which crystallises in slender, yellowish-red needles.

When benzoylphenylthiosemicarbazide is treated with benzoic chloride, it again loses the elements of water, but forms diphenylimidobiazolyl mercaptan, $HS\cdot C\!<\!\begin{matrix}NPh\cdot CPh\\ \quad\quad\ \ \| \\ N——N\end{matrix}$, which was also obtained by Pulvermacher, and is formed when benzoylphenylthiosemicarbazide is heated above its melting point. The *methiodide*, $C_{14}H_{11}N_3S,MeI$, forms white crystals, and when treated with alkalis yields the *base* $C_{15}H_{13}N_3S$, which crystallises in white needles melting at 164°. The *hydrochloride* melts at 161°, and the *sulphate* at about 250°, both salts being sparingly soluble in water. The *platinochloride* is a crystalline precipitate, and the *picrate* melts at 137°. The base is converted by oxidation with potassium permanganate into the corresponding *sulphone*, $SO_2Me\cdot C\!<\!\begin{matrix}NPh\cdot CPh\\ \quad\quad\ \ \| \\ N——N\end{matrix}$, which crystallises in matted needles melting at 176°. This proves that the methylated compound is a sulphide, and the original substance a mercaptan. When the latter is heated with dilute nitric acid, the sulphur is removed as sulphuric acid and *diphenylimidobiazole*, $CH\!<\!\begin{matrix}NPh\cdot CPh\\ \quad\quad\ \ \| \\ N——N\end{matrix}$, is formed; this melts at 142°. The *platinochloride* decomposes at about 160°, and the *picrate* melts at 174°.

A. H.

Identity of Formopyrine and Methylenebiantipyrine. By GUIDO PELLIZZARI (*Gazzetta*, 1896, **26**, ii, 407—412).—The author shows, by chemical and crystallographical comparisons, that Marcourt's formopyrin (*Bull. Soc. Chim.*, [3], **15**, 520) is identical with his own methylenebiantipyrine (Abstr., 1890, 645).

W. J. P.

Monosubstituted Triazoles. By GUIDO PELLIZZARI and C. MASSA (*Gazzetta*, 1896, **26**, ii, 413—429).—Formylparatolylhydrazide gradually separates from a solution of tolylhydrazine in ethylic formate (compare Ruhemann, Trans., 1890, 50). On slowly heating its hydrochloride with formamide to 200°, ammonia and water are evolved, and the residue, after treatment with potash solution, is extracted with

ether; a good yield of 1-*paratolyltriazole*, $\genfrac{}{}{0pt}{}{\text{CH:N}}{\text{N:CH}}\!\!>\!\text{N}\cdot\text{C}_6\text{H}_4\text{Me}$, is obtained on evaporating the ethereal solution. The triazole forms a white, crystalline mass, which melts at 67° and boils at 265°; it is volatile in a current of steam, has an odour of pyridine, and is soluble in ether, alcohol, benzene, or chloroform, but insoluble in water. It is also obtained on distilling a mixture of the formyltolylhydrazide with formamide. The *platinochloride*, $(C_9H_9N_3)_2,H_2PtCl_6$, crystallises in yellow needles, and when boiled with water or heated at 150—175°, yields *tetrachloroplatoparatolyltriazole*, $(C_9H_9N_3)_2,PtCl_4$, as an insoluble, yellow powder; when heated at 175—200°, it seems to give *dichloroplatoparatolyltriazole*, $(C_9H_7N_3)_2PtCl_2$, but this substance could not be obtained pure.

1-*Orthotolyltriazole*, prepared in a similar manner from orthotolylhydrazide hydrochloride, is a colourless substance which melts at 45°, boils at 270°, and resembles its para-isomeride. The *platinochloride* crystallises in yellow needles, and on boiling with water or heating at 150—180°, is converted into *tetrachloroplatorthotolyltriazole*; it decomposes on prolonged heating at 200°.

1 : *α-Naphthyltriazole*, $\genfrac{}{}{0pt}{}{\text{CH:N}}{\text{N:CH}}\!\!>\!\text{N}\cdot\text{C}_{10}\text{H}_7$, is prepared by gradually heating a mixture of α-naphthylhydrazide hydrochloride with formamide to 200°; formyl-α-naphthylhydrazide is formed as an intermediate product. The triazole crystallises from boiling water in lustrous, white needles, melting at 99°; it is odourless, and soluble in alcohol or chloroform. The *platinochloride*, $(C_{12}H_9N_3)_2,H_2PtCl_6$, forms small, yellow crystals, and on boiling with water, or heating at 160°, yields *tetrachloroplato-α-naphthyltriazole*, $(C_{12}H_9N_3)_2PtCl_4$, as a yellow, insoluble powder; on further heating, it is probably converted into the dichloro-compound by loss of 2HCl, but the product could not be purified.

1 : *β-Naphthyltriazole*, prepared by heating β-naphthylhydrazide hydrochloride with formamide at 120—150°, forms white crystals melting at 111°, and is rather more basic in properties than the preceding triazoles. The *platinochloride* crystallises in yellow needles and yields *tetrachloroplato-β-naphthyltriazole* as an insoluble, yellow powder when boiled with water or heated at 160—175°.

Orthotriazolebenzoic acid, $\genfrac{}{}{0pt}{}{\text{CH:N}}{\text{N:CH}}\!\!>\!\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{COOH}$, is prepared by oxidising orthotolyltriazole with alkaline permanganate at 100°; after separating the manganese dioxide, it is precipitated by sulphuric acid and crystallises from alcohol in minute, white crystals melting at 264°. It is soluble in hot alcohol, but nearly insoluble in hot water; the *barium* salt $(C_9H_9N_3O_2)_2Ba$, is very soluble in water, whilst the *copper* salt is blue and insoluble.

Paratriazolebenzoic acid is prepared in like manner, and forms minute crystals which do not melt at 270°; the *barium* salt is sparingly soluble.

W. J. P.

The Proteids of the Kidney Bean (Phaseolus vulgaris). By THOMAS B. OSBORNE (*J. Amer. Chem. Soc.*, 1894, 16, 757—764. Com-

pare Abstr., 1895, i, 454).—Phaseolin (*loc. cit.*) probably forms about 20 per cent. of the seed, the mean of 24 analyses gives the percentage composition as C = 52·58, H = 6·84, N = 16·47, S = 0·56, and O = 23·55.

Phaselin (*loc. cit.*) is slowly coagulated by heat at temperatures varying with the amount of salts present, and with the rapidity of heating. It is precipitated by acids; on prolonged dialysis yields insoluble or albuminate modifications, and has more nearly the properties of a globulin than of any other class of proteids. Its percentage composition (mean of 11 determinations) is C = 51·6, H = 7·02, N = 14·65, S = 0·49, and O = 26·24.

A small amount of *proteose* was also found in the extract.

J. J. S.

Hydrochloric Acid Compounds of Albumoses and Peptone. By OTTO COHNHEIM (*Zeit. Biol.*, 1896, **33**, 489—520).—The various albumoses and peptone differ from one another in the amount of hydrochloric acid with which they combine. In a 2·5 per cent. solution, they unite with hydrochloric acid, in percentages of their own weight, as follows: proto-albumose, 4·3; dentero-albumose, 5·5; hetero-albumose, 8·2; and antipeptone, 16 per cent. The proportion does not correspond exactly to any of the known properties of these substances, such as diffusibility, precipitability, &c. Probably the albumoses unite in different ways with the acid, some being more basic than others.

W. D. H.

Carbohydrate Group in the Albumin Molecule. By N. KRAWKOFF (*Pflüger's Archiv.*, 1896, **65**, 281—298).—Egg-albumin is freed with difficulty from ovo-mucoid, but the purest specimens obtained always yielded, after treatment with mineral acid, a reducing substance which gives with phenylhydrazine a crystalline osazone melting at 183—185° (Pavy gives 189—190°). The exact nature of this carbohydrate is not yet determined, but the main fact of its existence confirms the recent work of Pavy. No evidence, however, was found that artificial digestion of proteid leads to its appearance. Acid-albumin, alkali-albumin, commercial peptone, fibrin, serum-albumin, serum-globulin (slightly), lact-albumin (in traces) yield the same material. Casein, gelatin, vitellin, and nucleo-proteids from peas gave a negative result. Albumin from peas yielded an osazone with rather different characters.

W. D. H.

Chemical Structure of Hæmin and Hæmatin prepared by various methods. By M. BIALOBRZESKI (*Ber.*, 1896, **29**, 2842—2851).—The author confirms the formula

$$(C_{32}H_{31}N_4FeO_3Cl)_4,C_5H_{12}O,$$

given by Nencki and Sieber (Abstr., 1885, 70, 825) for the crystals of hæmin deposited from amylic alcohol. The mother liquors from the crystals obtained from the blood of horses by Nencki and Sieber's method give a mixture of substances partially soluble in ether; the soluble portion, which is an amorphous violet mass, dissolves readily in chloroform, alcohol, and alkalis, whilst the insoluble part is distinguished from hæmin by its greater stability towards nitric acid. Both portions, when dissolved in chloroform, give absorption spectra identical with that shown by hæmin in acid solution, but contain a higher per-

centage of carbon and hydrogen, the portion soluble in ether being somewhat poorer in iron content.

Hæmatin is readily obtained from the crystalline hæmin by treating it with a cold 10 per cent. solution of sodium hydroxide or by prolonged boiling with water; its composition is represented by the formula $C_{32}H_{31}N_4FeO_3$.

The method used by Schalféeff (Abstr., 1885, 566) for the isolation of hæmin is a very productive one; the crystalline hæmin, finally obtained, contains acetic acid after desiccation over sulphuric acid, and its composition is best represented by the formula

$$(C_{32}H_{31}N_4FeO_3Cl)_3,C_{32}H_{31}FeN_4O_3\cdot OAc,HOAc,$$

whether obtained from the blood of horses, oxen, or dogs. When it is hydrolysed with boiling water, no acetic acid is liberated, but sodium acetate is obtained if the hydrolysis be effected by means of dilute soda. The substance yields hæmatoporphyrin on treatment with hydrogen bromide, and has the composition $C_{16}H_{18}N_2O_3,HCl$.

Hæmin, obtained by either of the foregoing methods, contains no appreciable quantity of xanthine; it is certain, therefore, that the iron content is to that of nitrogen in the ratio of one atom of the former to four of the latter, hence its formula cannot be that proposed by Cloetta. When treated with cold sulphuric acid or alcoholic hydrogen chloride, it loses both nitrogen and iron, and gradually alters in character, assuming the properties described by Cloetta, and becoming insoluble in alkali; the ratio of the nitrogen to iron, however, remains approximately constant. This behaviour does not appear to be due to the presence of a labile aldehyde group, as phenylhydrazine has no action on the substance.

Cloetta's hæmin is separable into two approximately equal parts by dissolving it in chloroform and subsequently precipitating with ether; the composition of the two portions is different, and it is probable that we are here dealing with decomposition products of hæmin, for if the mother liquors obtained in preparing the substance by Cloetta's method be extracted with chloroform, the residual aqueous solution, on spectroscopic examination, will reveal the presence of hæmatoporphyrin. It is clear, therefore, that Cloetta's process induces an undesirable decomposition of the hæmin, the product containing too little nitrogen and iron.

A. L.

Phrenosin. By ALBRECHT C. L. M. L. KOSSEL (*J. pr. Chem.*, 1896, [2], 54, 215—216).—A reply to Thudichum (Abstr., 1896, i, 400).

A. G. B.

Organic Chemistry.

Preparation of Cyanamide. By REINHOLD WALTHER (*J. pr. Chem.*, 1896, [2], 510—512.)—A solution of cyanamide may be prepared very easily by dissolving thiocarbamide in 10 or 20 per cent. aqueous potassium hydroxide, adding gradually a 30 per cent. lead acetate solution, and finally filtering from the precipitated lead sulphide; 5·5 grams of lead acetate, and about 3 grams of caustic potash are required per gram of thiocarbamide.

Cyanamide is much more stable in the presence of alkalis, and in solution generally, than is commonly supposed. On the other hand, the dry substance has a tendency to explode spontaneously. C. F. B.

Mercuric Chlorothiocyanate. By CHARLES H. HERTY and J. G. SMITH (*J. Amer. Chem. Soc.*, 1896, **18**, 906—908).—The authors have investigated the compound described by McMurtry as mercuric chlorothiocyanate (Trans., 1889, 50), and have come to the conclusion that it is a definite chemical compound, and not merely a mixture of mercuric thiocyanate and mercuric chloride. J. J. S.

1:3-Dibromopropene [$\alpha\gamma$-Dibromopropylene]. By ROBERT LESPIEAU (*Compt. rend.*, 1896, **123**, 1072—1073). — When a mixture of α-propenyl dibromhydrin and phosphoric anhydride is distilled, hydrogen bromide, tribromhydrin and β-epidibromhydrin, $CHBr{:}CH{\cdot}CH_2Br$, are obtained. The latter is a colourless liquid boiling at 155—156° and of sp. gr. $= 2{\cdot}097$ at 0°; it solidifies when cooled to $-75°$, and melts again at $-52°$. It is not formed in the action of caustic potash on propenyl tribromhydrin. It can be converted into an acetin boiling at 175—177°, from which *bromallylic alcohol*, $CHBr{:}CH{\cdot}CH_2{\cdot}OH$, boiling at 169—170°, and of sp. gr. $= 1{\cdot}59$ at 0°, can be obtained.

Methylic bromallylic ether boils at 127°, and *ethylic bromallylic ether* at 145°. All these compounds unite readily with two atoms of bromine, but in the case of the methylic ether substitution also occurs, and a new bromacrylic acid, $CHBr{:}CH{\cdot}COOH$, is formed, melting and decomposing at 140° (the two known isomerides melt at 115° and 70° respectively). Caustic potash removes 1 mol. HBr from these substances, giving rise to the corresponding acetylene compounds.

When β-epidibromhydrin is vigorously shaken with an aqueous solution of potassium cyanide, *bromocrotononitrile*, $CHBr{:}CH{\cdot}CH_2{\cdot}CN$, is formed, boiling at 95—98° (23 mm.), and from this *γ-bromocrotonic acid*, $CHBr{:}CH{\cdot}CH_2{\cdot}COOH$, melting at 58—59°, can be obtained. A. C. C.

Polymerisation of Olefine Hydrocarbons, I and II. By IWAN L. KONDAKOFF (*J. pr. Chem.*, 1896, [2], **54**, 442—454; 454—468).—Some zinc chloride was placed in a sealed tube, tertiary butylic chloride (1 mol.) added, the tube cooled to $-18°$, and isobutylene (1 mol.) passed in; the tube was then sealed, and allowed to remain at the ordinary temperature. The tertiary butylic chloride was obtained by allowing hydrochloric acid, saturated at 0°, to act on isobutylene in a sealed tube;

the isobutylene being prepared from isobutylic iodide and alcoholic potash. The zinc was used in amount equal to 10 per cent. of the hydrocarbon; if a larger quantity is used, the reaction is more rapid and energetic, but much larger quantities of tributylene, and even some tetrabutylene, are formed. After unchanged isobutylene and tertiary butylic chloride had been distilled off on the water-bath from the product of the reaction, and the residue had been freed from zinc by treatment with dilute acid, it was found best to treat it with moist silver oxide; an isodibutylene (octylene), and a little isotributylene then remained undissolved, whilst isodibutyl and tertiary butylic alcohol dissolved in the water, these resulting respectively from the action of the silver oxide on octylic chloride and on the residuary tertiary butylic chloride. The octylene boils at 101°—101·7°, and has a sp. gr. = 0·7326 at 0°/0°, and 0·7158 at 21°/21°; the isomeric substance obtained by Butleroff by the action of sulphuric acid on tertiary butylic alcohol boils at a temperature 1° higher, and has a sp. gr. = 0·7360 at 0°, but both substances yield the same derivatives when heated in a sealed tube at 100° with halogen acids saturated at −20°; the *octylic* (isodibutylic) *chloride* thus obtained boils at 40° under 13 mm. pressure, and has a sp. gr. = 0·8891 at 0°/0°, and 0·8756 at 18°/18°; the *bromide* boils at 62° under 18 mm. pressure and has a sp. gr. = 1·0634 at 0°/0°, and 1·0471 at 18°/18°; the *iodide* boils at 108—109° under 15 mm. pressure, and has a sp. gr. = 1·1122 at 0°/0°, and 1·0955 at 17°/17°. Probably both substances are mixtures of the two octylenes, the formation of which might be expected, namely $CH_2{:}CMe{\cdot}CH_2{\cdot}CMe_3$ and $CMe_2{:}CH{\cdot}CMe_3$, the first of these forming the chief constituent of Butleroff's substance, the second of the author's product. In the reaction studied by the author, the zinc chloride probably first forms a compound with the isobutylene; this then reacts with the tertiary butylic chloride, forming an octylic chloride, from which isobutylene withdraws hydrogen and chlorine, octylene and tertiary butylic chloride being produced.

"Trimethylethylene" and tertiary amylic chloride were allowed to react in the presence of zinc chloride, in the manner described above, except that the mixture was placed in flasks, instead of in sealed tubes. The tertiary amylic chloride was obtained by the action of hydrochloric acid, saturated at 0°, on "trimethylethylene." The latter was prepared by three different methods: by treating tertiary amylic alcohol with dilute sulphuric acid, or with oxalic acid, or by decomposing tertiary amylic iodide with alcoholic potash. The reaction takes place in the same way as with the butyl compounds. A diamylene (decylene), $C_{10}H_{20}$, was obtained; this boils at 154—159°, and has a sp. gr. = 0·7836 at 0°. It is apparently identical with the substance obtained by Erlenmeyer and by Wischnegradsky by acting on fermentation amylic alcohol with sulphuric acid; this substance boils at 154—159°, and has a sp. gr. = 0·7833 at 0°. When treated with halogen acids, both substances yield the same *decylic chloride*, boiling at 87—89° under 19 mm. pressure, and of sp. gr. 0·9011 at 0°/0° and 0·8894 at 14·5°/14·5°; *bromide*, boiling at 99—101° under 18 mm. pressure, and of sp. gr. 1·0420 at 0°/0° and 1·0071 at 18°/18°; and *iodide*, boiling at 114—116° under 16 mm. pressure, and of sp. gr. 1·2490 at 0°/0°, and 1·2340 at 14·5°/14·5°. All these compounds regenerate the original decylene when they are treated with alcoholic potash. Further, when the iodide is treated with moist silver

oxide, *diamylene hydrate*, $C_{10}H_{21}\cdot OH$, is formed; this boils at 191—192°, and has a sp. gr. = 0·8380 at 0°/0°; it has the properties of an alcohol, and with phenylcarbimide yields a *phenylcarbamate*, which sublimes at 214° without melting, and crystallises from a mixture of alcohol and ethylic acetate in two forms, needles and short prisms. This points to the possibility of the decylene being really a mixture, which is all the more likely, as "trimethylethylene," which served as the starting-point, is known to contain unsymmetrical methylethylethylene. Very probably, the decylene consisted of $CMe_2\colon CMe\cdot CMe_2Et$, formed from trimethylethylene, and $CMe_2Et\cdot CH\colon CMeEt$, formed from methylethylethylene. A certain confirmation of this view was obtained, for methylethylcarbincarbinol, separated by Le Bel's method from the isobutylcarbinol that occurs mixed with it in fermentation amylic alcohol, was converted into the iodide, and then into methylethylethylene. This methylethylethylene boiled at 31—32°, and, with tertiary amylic chloride and zinc chloride, yielded a decylene which boiled at 157—157·5° under 759 mm. pressure, and had a sp. gr. = 0·7878 at 0°/0° and 0·7729 at 21°/21°. C. F. B.

Invert-Sugar, I and II. By JOHN HERON (*J. Fed. Inst. Brewing*, 1896, **2**, 440—452; 457—482). See this vol., ii, 194.

Preparation of Fatty Amines. By AUGUSTE TRILLAT (*Bull. Soc. Chim.*, 1896, [3], **15**, 321—322).—The author takes exception to Brochet's reply to his criticism of the conclusions drawn by Brochet and Cambier from their work on this subject. (Compare Abstr., 1896, i, 407.)

M. W. T.

Action of Methylic Alcohol on Magnesium Nitride. By EMERICH SZARVASY (*Ber.*, 1897, **30**, 305—309).—Methylic alcohol reacts energetically with magnesium nitride, and whether the two are heated at 270° in a sealed tube, or no extraneous heat is applied, large quantities of ammonia, trimethylamine, and hydrogen are produced, together with a solid residue of indefinite constitution.

If, however, the compounds are allowed to react in a flask, fitted with a reflux condenser, and cooled in a freezing mixture, the evolved gases can be collected, and the proportions in which they are produced determined; this is found to be 40 per cent. of trimethylamine and 60 of ammonia.

The residue in the flask is a white, porous substance closely resembling magnesium oxide, which, from its analyses and reactions, is evidently *magnesium hydroxide methoxide*, $Mg(OH)\cdot OMe$, the action of the nitride on the alcohol being represented by the equation

$$Mg_3N_2 + 6MeOH = 3Mg(OH)\cdot OMe + NH_3 + NMe_3.$$

Magnesium hydroxide methoxide is decomposed by water at the ordinary temperature, with production of magnesium hydroxide and methylic alcohol, whilst when dissolved in acids the corresponding magnesium salt and methylic alcohol are obtained. J. F. T.

Action of Hydroxylamine on Phorone. By CARL D. HARRIES and FRITZ LEHMANN (*Ber.*, 1897, **30**, 230—234).—The authors have submitted phorone to the action of hydroxylamine, and failed to obtain the normal oxime described by Naegeli (Abstr., 1883, 728); according to the experimental conditions, however, they have obtained three new substances.

Triacetonehydroxylamine, $CO<\begin{matrix}CH_2\cdot CMe_2\\CH_2\cdot CMe_2\end{matrix}>NOH$, is prepared by heating phorone with alcoholic hydroxylamine (1 mol.) for 24 hours on the water bath; it crystallises from light petroleum, and melts at 50—51°. It dissolves readily in concentrated acids, and is precipitated from the solutions by alkalis; a cold, ammoniacal silver solution is reduced by the substance, and Fehling's solution when heated with it. The *hydrochloride* is crystalline. The *oxime*,

$$OH\cdot N\cdot C<\begin{matrix}CH_2\cdot CMe_2\\CH_2\cdot CMe_2\end{matrix}>N\cdot OH,$$

crystallises from light petroleum, and melts at 126—127°; it reduces Fehling's solution when heated.

The *base*, $C_9H_{18}N_2O_2$, is obtained by heating phorone with two molecular proportions of hydroxylamine, and when crystallised from light petroleum melts at 101—102°; it does not form an oxime, and is indifferent towards boiling Fehling's solution. The *hydrochloride* crystallises in small needles, and melts and decomposes at 165°; the *diacetyl* derivative crystallises from light petroleum in leaflets, and melts at 141°.

The action of hydroxylamine on mesitylic oxide has also been investigated. M. O. F.

Synthesis of β-Hydroxy Acids. By SERGIUS N. REFORMATSKY (*J. pr. Chem.*, 1896, [2], **54**, 469—477).—This paper is a summary of results obtained by the author and his students, and already published in detail in the *J. Russ. Chem. Soc.* and in the *Berichte.* Evidence is now available to show that the action of zinc on a mixture of a halogen fatty acid, $CR^1R^2X\cdot COOR^3$ [R^1, R^2, R^3 = alkyl radicles or hydrogen, X = Cl, Br, or I], with a ketone, aldehyde, or formate, CR^4R^5O, [in this case R^5 may = OEt when R^4 = H; the R's may also be aromatic radicles] results in the successive formation of the following compounds, as representatives of all of these compounds have been isolated:—(1) $X\cdot Zn\cdot CR^1R^2\cdot COOR^3$; (2) $X\cdot Zn\cdot O\cdot CR^4R^5\cdot CR^1R^2\cdot COOR^3$; (3) $OH\cdot CR^4R^5\cdot CR^1R^2\cdot COOR^3$.

In the case of ethylic formate, the third stage is different, the compound (2) $X\cdot Zn\cdot O\cdot CH(OEt)\cdot CR^1R^2\cdot COOR^3$ yielding (3) $X\cdot Zn\cdot O\cdot CH(CR^1R^2\cdot COOR^3)_2$, and this (4) $OH\cdot CH(CR^1R^2\cdot COOR^3)_2$.

In carrying out the reaction, the mixture of the ethylic salt of the halogen acid with the carbonyl compound was poured on to dry zinc, and allowed to remain until the odour of these substances had disappeared; water and dilute sulphuric acid were then added. The duration of the action varied from a few hours to several months, the yield being from 25 to 95 per cent. Ethylic chloracetate gave the best yields with ketones, but would not react with aldehydes. The other ethereal salts reacted readily with aldehydes, especially benzaldehyde, but only with difficulty with ketones, acetone excepted. The rule observed by Bischoff, that compounds containing many methyl groups in proximity are only formed with difficulty, was not confirmed by these researches, which lead but to the conclusion that "no definite generalisation can yet be made regarding the dynamic influence which the different groups exercise on the course of the reaction." C. F. B.

The Decomposition of β-Monhydroxy-acids. By SERGIUS N. REFORMATSKY (*J. pr. Chem.*, 1896, [2], 477—481).—A study has been made of the decomposition that 19 β-hydroxy-acids undergo, under the influence of sulphuric acid, of hydriodic acid, and when heated alone. The following are the generalisations made.

"As a rule, they lose water and form unsaturated acids, the water being formed from the hydroxyl group, and a hydrogen atom in the α- or γ-position, it is immaterial which; in the latter case, the βγ-unsaturated acid formed undergoes a further transformation into the lactone [$CHMe_2 \cdot CH(OH) \cdot CHMe \cdot COOH \rightarrow CHMe_2 \cdot CH{:}CMe \cdot COOH$, and $CMe_2{:}CH \cdot CHMe \cdot COOH$, or rather the corresponding lactone,

$$CMe_2 \lt \begin{matrix} CH_2 \cdot CHMe \\ \overline{\quad O \quad} \end{matrix} \gt CO].$$

"If there is no hydrogen atom, either in the α- or in the γ-position, the aliphatic hydroxy-acids decompose into an aldehyde and an unsaturated acid ($OH \cdot CHMe \cdot CEt_2 \cdot COOH \rightarrow CHMeO + CHEt_2 \cdot COOH$); the aromatic ones yield a hydrocarbon, ($OH \cdot CHPh \cdot CMe_2 \cdot COOH \rightarrow CHPh{:}CMe_2$); and the tertiary ones an alcohol and a hydrocarbon, ($OH \cdot CMe_2 \cdot CMe_2 \cdot COOH \rightarrow OH \cdot CMe_2 \cdot CHMe_2$ and $CMe_2{:}CMe_2$).

"Of the secondary hydroxy-acids containing the group CH in the α-position, the only ones that do not yield an unsaturated acid are those which contain the group $OH \cdot CHPh$; these, under the influence of sulphuric acid, decompose into carbonic anhydride and a hydrocarbon of the series C_nH_{2n-8}.

$$(OH \cdot CHPh \cdot CHMe \cdot COOH \rightarrow CO_2 + H_2O + CPh{:}CHMe)."$$

C. F. B.

Stereoisomerism of Ethylic Isonitrosoacetoacetate. By MILORAD Z. JOVITSCHITSCH. (*Bull. Soc. Chim.*, 1896, [4], **15**, 221—227). —The author has already pointed out (Abstr., 1896, 81, 82) the existence of two stereoisomeric forms of the compound $COMe \cdot C(N \cdot OH) \cdot COOEt$. These compounds could only be distinguished by the manner in which they behave when treated with potash, but he now brings forward further facts with regard to the relationship between them (Abstr., 1896, i, 81). When treated with 1 molecule of bromine, the bromine seems to displace an atom of hydrogen in the methyl group in the case of the *anti*-derivative, and, in the oximido-group, in the case of the *syn*-derivative. A second molecule of bromine displaces a hydrogen atom in the oximido-group of the *anti*-derivative, and in the methyl group of the *syn*-derivative. The substitution of bromine for hydrogen in the oximido-group is accompanied by a violent action.

The paper concludes with a note on the preparation of the isomeric ethylic isonitrosoacetoacetates. M. W. T.

Action of Fuming Nitric Acid on Ethylic Acetoacetate. By WALTER BECKH (*Ber.*, 1897, **30**, 152—156).—*Ethylic ββ-Dioximidosuccinate* which is best prepared by the etherification of Söderbaum's ββ-dioximidosuccinic acid, using the silver salt, is a crystalline compound, separating from ether, on the addition of light petroleum, as a fine powder, melting at 162°. On oxidation with

gaseous nitrous anhydride, it yields *ethylic glyoximeperoxidedicarboxylate*, $COOEt\cdot C\underset{O\cdot N}{\overset{N\cdot O}{\lessgtr}}C\cdot COOEt$, which is in every respect identical with the compound $C_8H_{10}N_2O_6$, obtained by Pröpper by the action of fuming nitric acid on ethylic acetoacetate. Pröpper did not obtain a sharp boiling point for this compound, but the author finds that it boils constantly at 159° under a pressure of less than 10 mm., whereas if the pressure is greater than this, no fraction of constant boiling point can be obtained. J. F. T.

Moniodosuccinic Acid. By HEINRICH BRUNNER and ERNEST CHUARD (*Ber.*, 1897, **30**, 200—201. Compare Abstr., 1886, 576).—The salts of the moniodosuccinic acid, which is prepared by heating monobromosuccinic acid with alcoholic potassium iodide, are identical with those of the acid previously obtained by the authors by the action of iodine on the juices of certain fruits and plants. The free acid could not be obtained, since it decomposes, with formation of fumaric acid, when its solutions are evaporated. A. H.

Action of Phenylcarbimide on γ-Pimelic Acid derived from Menthol. By GEORGES ARTH (*Bull. Soc. Chim.*, 1896, [4], **15**, 227—229).—Mehrländer has attempted to prove that the acid, $C_7H_{12}O_4$, which is obtained among the oxidation products of menthol, is identical with propylsuccinic acid. The author has shown that this is probably not the case, as the acid derived from menthol does not form an anhydride.

To confirm this view, he treated the latter acid with phenylcarbimide, and obtained its dianilide, but as this product did not give a phenylimide, $C_5H_{10}{:}(CO)_2{:}NPh$, on heating, he concludes that the original acid is incapable of forming an anhydride. (Compare Haller, Abstr., 1892, 1204). M. W. T.

Normal-Dilevulinic Acid (4 : 7-Decandiondioic Acid). By EDUARD A. KEHRER and ERWIN HOFACKER (*Annalen*, 1896, **294**, 165—182. Compare Abstr., 1895, i, 334).—*Normal dilevulinic (4 : 7-decandiondioic) acid*, $C_2H_4(CO\cdot CH_2\cdot CH_2\cdot COOH)_2$, is produced on heating δ-furfurylidenelevulinic acid with alcohol and concentrated hydrochloric acid for 2—3 hours in a reflux apparatus; it crystallises from water in lustrous, snow-white leaflets, and melts at 156—157°. The *ammonium* salt is crystalline, the *calcium* salt forms needles containing $2H_2O$, and the *hydrogen calcium* salt is anhydrous; the *barium* salt is microcrystalline, and contains $1H_2O$, and the methylic salt crystallises from water and melts at 98° (compare *loc. cit.*). The *phenylhydrazone* melts at 111—112°, and the *oxime* crystallises in colourless prisms and melts at 164—165°; the *silver* derivative of the oxime is amorphous. The *phenylhydrazone* and *oxime* of the methylic salt melt at 105° and 108—109° respectively; the *phenylhydrazone* and *oxime* of the ethylic salt melt at 104—105° and 129—130° respectively.

When normal dilevulinic acid is oxidised with nitric acid of sp. gr. = 1·3, the main product is succinic acid—small quantities of oxalic acid and hydrogen cyanide, along with a trace of formic acid, being also produced. M. O. F.

Derivatives of Pentamethylene and R-Pentene. By LUDWIG WOLFF and FRITZ RÜDEL (*Annalen*, 1896, **294**, 183—205).—2 : 2-*Dibromo*-1 : 3-*diketo*-R-*pentene*, $\begin{array}{l}\mathrm{CH\cdot CO} \\ \| \\ \mathrm{CH\cdot CO}\end{array}\!\!>\!\mathrm{CBr_2}$, is obtained by heating dibromolevulinic acid with 6 parts of a mixture of fuming sulphuric (1 part) and Nordhausen (3 parts) acids for 20 minutes at the temperature of boiling water; it crystallises from alcohol in rectangular plates, and melts at 137°.

2 : 4-*Dibromo*-1 : 3-*diketo*-R-*pentene*, $\begin{array}{l}\mathrm{CBr\cdot CO} \\ \| \\ \mathrm{CH\cdot CO}\end{array}\!\!>\!\mathrm{CHBr}$, is produced when the dibromo-acid is heated with 4 parts of a mixture of concentrated sulphuric and Nordhausen acids in equal proportions, and crystallises in white needles melting at 98·5—99°; the *azine* is obtained by treating the substance with an alcoholic solution of orthophenylenediamine, and crystallises from benzene in red needles melting at about 180°. Dichlorolevulinic acid yields the dichlorodiketopentene (m. p. 89°) described by Zincke and Fuchs (Abstr., 1893, i, 319).

2 : 2 : 4 : 5-*Tetrabromodiketopentamethylene*, $\begin{array}{l}\mathrm{CHBr\cdot CO} \\ | \\ \mathrm{CHBr\cdot CO}\end{array}\!\!>\!\mathrm{CBr_2}$, is obtained by the action of bromine on 2 : 2-dibromodiketopentene dissolved in carbon bisulphide, and crystallises from petroleum in needles melting at 83°.

2 : 2 : 4-*Tribromodiketo*-R-*pentene*, $\begin{array}{l}\mathrm{CBr\cdot CO} \\ \| \\ \mathrm{CH{-}{-}CO}\end{array}\!\!>\!\mathrm{CBr_2}$, arises from the tetrabromo-derivative under the influence of alcoholic sodium acetate (2 mols.); it crystallises from hot alcohol in lustrous leaflets, and melts at 120°.

2 : 2 : 4-*Tribromo*-5-*hydroxydiketopentamethylene*, $\begin{array}{l}\mathrm{CHBr{-}{-}CO} \\ | \\ \mathrm{CH(OH)\cdot CO}\end{array}\!\!>\!\mathrm{CBr_2}$, is produced when the tetrabromo-derivative is heated with 90 per cent. acetic acid; it crystallises in lustrous prisms, and melts at 146°.

2 : 4 : 4 : 5-*Tetrabromodiketopentamethylene*, $\begin{array}{l}\mathrm{CBr_2{-}{-}CO} \\ | \\ \mathrm{CHBr\cdot CO}\end{array}\!\!>\!\mathrm{CHBr}$, is obtained from the 2 : 4-dibromodiketopentene by the action of bromine, and crystallises from petroleum in long needles melting at 87°; alcoholic sodium acetate converts it into 2 : 4 : 5-*tribromodiketo*-R-*pentene*, $\begin{array}{l}\mathrm{CBr\cdot CO} \\ \| \\ \mathrm{CBr\cdot CO}\end{array}\!\!>\!\mathrm{CHBr}$, which crystallises from alcohol in prismatic needles and melts at 116·5°. When the tetrabromo-derivative is heated with methylic alcohol, a *methoxy*-compound is produced, and separates from petroleum in prismatic crystals melting at 126°.

Oxidation of 2 : 2-dibromodiketo-R-pentene with dilute nitric acid gives rise to dibromodinitromethane, along with fumaric and tribromacetylacrylic acids.

Tribromacetylacrylic acid, $\mathrm{CBr_3\cdot CO\cdot CH{:}CH\cdot COOH}$, crystallises from chloroform in small, white needles, sinters at 149°, and, when rapidly heated, melts at 156°; when heated with sodium carbonate, bromoform is eliminated, and maleic acid produced.

Tetrabromacetylacrylic acid, $CBr_3 \cdot CO \cdot CBr \colon CH \cdot COOH$ or $CBr_3 \cdot CO \cdot CH \colon CBr \cdot COOH$, is formed by the action of hypobromous acid on 2 : 2-dibromodiketo-R-pentene or by treating 2 : 2 : 4-tribromodiketo-R-pentene with dilute nitric acid ; it crystallises from hot water in prisms or needles, and melts at 160°.

Oxidation with 16 per cent. nitric acid converts 2 : 4-dibromodiketo-R-pentene into tribromonitromethane and bromofumaric acid.

βδ-dibromolevulinic anhydride is obtained by heating dibromolevulinic acid with acetic anhydride ; it crystallises from benzene in slender, white needles, and melts indefinitely at 138°. When heated with acetic anhydride for a long period of time, the substance yields an oily, neutral product, which gives rise to a small quantity of a crystalline substance when submitted to distillation ; this compound melts at 87°, and has the composition of a tribromodiketopentamethylene, $C_5H_3Br_3O_2$. M. O. F.

Derivatives of Butyltoluene. By ALBERT BAUR (THURGAU) (*Ber.*, 1897, **30**, 303—305).—When acetobutylorthotoluidide, melting at 164°, is nitrated, two products are formed. The *mononitro*-derivative melts at 147°, and is more soluble than the *dinitro*-derivative, which crystallises in needles and melts at 199°. The *mononitro*-base, obtained on hydrolysis, crystallises in brownish-red tablets, and melts at 81°, whilst the *dinitro*-base melts at 131°. The mononitro-base, on reduction, yields an amidobutyltoluidine, and this readily reacts with phenanthraquinone, forming a *phenazine*-derivative, which melts at 153°. The constitution of the mononitro-base is, therefore,

$$[Me : C_4H_9 : NO_2 : NH_2 = 1 : 3 : 5 : 6].$$

When it is diazotised, and the filtered solution boiled with alcohol, *mononitrobutyltoluene* $[Me : C_4H_4 : NO_2 = 1 : 3 : 5]$ is obtained as an oil which melts at 32° and boils at 120° (pressure = 15 mm.). Nitric acid converts it into a mixture of nitrocarboxylic acids. Mononitrobutyltoluene is accompanied by a *trinitrobutyltoluidine* which melts at 168°, and yields a *monethyl* derivative melting at 113°. Energetic nitration of the trinito-base yields an acid explosive substance which appears to have the formula $C_6(NO_2)_5 \cdot NH \cdot NO$. A. H.

Benzoyldiazobenzene. By ARTHUR R. HANTZSCH and MARTIN SINGER (*Ber.*, 1897, **30**, 319—320).—In continuing their researches on the diazosulphones, the authors have had occasion to deal with E. Fischer's benzoyldiazobenzene, and although they have been unable to obtain any results bearing on the stereochemistry of the diazo-compounds, yet they have observed that it unites with gaseous hydrogen chloride, forming *benzoylorthochlorophenylhydrazine* ; this crystallises from boiling alcohol in white crystals melting at 152°.

The constitution of the compound follows from the fact that it yields benzoic acid and orthochlorophenylhydrazine on treatment with concentrated hydrochloric acid. J. F. T.

Conversion of Phenylhydrazine into Diazobenzene by Nitrous Acid. by JULIUS ALTSCHUL (*J. pr. Chem.*, 1896, [2], **54**, 496—508.)—

Nitrous acid, in the cold and in the presence of a strong mineral acid, oxidises phenylhydrazine to diazobenzene. For instance, 0·145 gram of pure phenylhydrazine hydrochloride was dissolved in 20 c.c. of water, the solution cooled, 2 c.c. of a di-normal sodium nitrite solution added, and then a mixture of 0·5 c.c. of strong hydrochloric acid with 2 c.c. of water; after an interval of 10 minutes or so, it was found that 80 per cent. of the phenylhydrazine had been converted into diazobenzene. This was ascertained by extracting the liquid twice with ether, to remove nitrosophenylhydrazine, and pouring it into an excess of a N/10 solution of sodium β-naphtholdisulphonate ("R-salt"), the excess of which was then titrated with a N/10 diazotoluene solution. The diazobenzene is formed by the direct action of the nitrous acid on the phenylhydrazine, and not by the decomposition, theoretically possible, of nitrosophenylhydrazine first formed into diazobenzene and hydroxylamine, for a solution of nitrosophenylhydrazine in cold hydrochloric acid gives no azo-dye when poured into the R-salt solution.

C. F. B.

Diazotisation of Aniline in the presence of Acetic Acid, or of an Insufficient Amount of Hydrochloric Acid. By JULIUS ALTSCHUL (*J. pr. Chem.*, 1896 [2], **54**, 508—510).—Aniline is diazotised to the extent of about 20 per cent. in the presence of $2\frac{1}{2}$ mols. of acetic acid, completely in the presence of 11 mols.

Aniline hydrochloride is diazotised only partially by sodium nitrite if no excess of acid is added. The diazotisation increases with the concentration of the solution; in solutions containing, respectively, 10, 1, and 0·1 per cent. of aniline, about 30, 20, and 10 per cent. of the aniline was diazotised.

C. F. B.

Action of Bleaching Powder Solution on Phenylhydrazine. Formation of Azobenzene. By HEINRICH BRUNNER and LOUIS PELET (*Ber.*, 1897, **30**, 284—285).—When phenylhydrazine is treated with bleaching powder solution, azobenzene and benzene are formed; in the early stages of the reaction a smell of nitrobenzene is noticed.

A. H.

Comparative Experiments with Normal and Iso-diazotates. By EUGEN BAMBERGER (*Ber.*, 1897, **30**, 211—219. Compare Abstr., 1896, i, 299).—As shown by von Pechmann (Abstr., 1894, i, 282), normal diazobenzene sodium and diazoparatoluene sodium, when acted on by acid chlorides, are converted into the nitroso-derivative of the corresponding acid anilide. The potassium salts behave in a similar manner, normal diazobenzene potassium and normal diazoparatoluene potassium being converted by benzoic chloride into nitrosobenzanilide and nitrosobenzotoluidide. The iso-salts, however, do not undergo this change, but are converted into the normal salts, a very small amount of the nitrosoanilide being sometimes formed from these by the action of the chloride or anhydride. It seems probable that the iso-salt first reacts in the sense of the equation,

$$PhN_2\cdot OK + ClCOPh = PhN_2Cl + Ph\cdot COOK,$$

and that the diazonium chloride thus produced is converted into the normal diazo-salt by the alkali present. This is confirmed by the fact that, when isodiazobenzene potassium and picric chloride are brought

together in alcoholic solution, a considerable amount of potassium picrate is precipitated, whilst the filtrate reacts with β-naphthol solution to form phenylazo-β-naphthol.

Behaviour of normal and isodiazotates towards sodium amalgam [with N. RONGGER]. When the potassium salts of isodiazobenzene and its substitution derivatives are treated with sodium amalgam, they yield no hydrazine, or only a small amount, whereas the salts of the normal compounds yield a large proportion of hydrazine. The following table gives the experimental results obtained, the numbers in the two columns expressing the percentage of the theoretical yield of hydrazine which was actually produced. The potassium salt of isoparasulphodiazobenzene yields much more hydrazine than any of the other isocompounds, but still less than the corresponding normal salt.

		Normal	Iso.
Diazobenzene potassium	(1)	0	72
	(2)	0	75
Parachlorodiazobenzene potassium ...	(1)	7	74
	(2)	0	
Parabromodiazobenzene potassium ...	(1)	0	54
	(2)	0	
Parasulphodiazobenzene potassium ...	(1)	28	63
	(2)	31	70

Parachlorophenylhydrazine melts at 88°, and not at 83° as usually stated. *Acetone-parachlorophenylhydrazone* forms silvery white, flat needles which have a satiny lustre, and melt at 84°. It is rapidly converted into a resinous mass on exposure to the air.

A. H.

Diquinoyltrioxime and Tetranitrophenol. By RUDOLF NIETZKI and F. BLUMENTHAL (*Ber.*, 1897, **30**, 181—186).—*Diquinoyltrioxime*, $C_6H_2O(N\cdot OH)_3$, which is formed together with the tetroxime by the action of hydroxylamine hydrochloride on dinitrosoresorcinol, is distinguished from it by its insolubility in the usual indifferent solvents. It is purified by means of the *ammonium* salt, which crystallises in yellowish-red needles. The free oxime is a brownish-yellow, crystalline powder, which deflagrates at about 250° without melting; when treated in the cold with acetic anhydride, it is converted into a *diacetate* which melts at 142°, and cannot be recrystallised without undergoing decomposition. If this diacetate is heated with acetic anhydride, the *anhydride* of the oxime, $C_6H_3N_3O_3$, is formed; this crystallises in almost colourless, stellate groups of needles, melts at 181°, and gives an intense green coloration with ferrous salts. The *ferrous* salt, $(C_6H_4N_3O_4)_2Fe$, which is thus formed, can readily be isolated and recrystallised from ethylic acetate.

When the trioxime is treated with stannous chloride and hydrochloric acid, it is reduced to triamidophenol. The *sulphate* of this base, $C_6H_9N_3O,H_2SO_4$, is only very sparingly soluble in water; the *picrate* has also been prepared. Triamidophenol gives a blue coloration with ferric chloride; its *triacetyl* derivative melts at 230°, and the *tetracetyl* derivative at 211°.

It was found impossible to bring about a simple oxidation of the

trioxime. Dilute nitric acid, however, converts it into tetranitrophenol, $C_6H(NO_2)_4\cdot OH$, which probably has the asymmetric constitution, $[OH : (NO_2)_4 = 1 : 2 : 3 : 4 : 6]$; this crystallises in broad, golden-yellow needles, with a violet iridescence, and melts at 130°, often with a somewhat violent explosion. It dyes wool and silk a redder shade than picric acid. Its salts are extremely explosive; the *sodium* salt crystallises in reddish-yellow needles, the *barium* salt in dark yellow prisms, whilst the *silver* salt forms a reddish-yellow, crystalline precipitate. A. H.

A Law of Production of Phenolcarboxylic Chlorides. By RICHARD ANSCHÜTZ (*Ber.*, 1897, **30**, 221—223).—Study of the behaviour of hydroxybenzoic acids towards phosphorus pentachloride has led to the following generalisation. Orthohydroxybenzoic acids yield the free phenolcarboxylic chlorides on treatment with phosphorus pentachloride, when the second ortho-position with regard to the hydroxy-group is already occupied; if this is not the case, the phosphorus oxychloride derivative of the corresponding phenolcarboxylic chloride is produced. The following compounds have been prepared. 3-*Methyl*-, 3-*chloro*-, and 3-*nitrosalicylic chlorides*, melting at 27—28°, 62—63°, and 60° respectively; 3 : 5-*dichloro*-, 3 : 5-*dibromo*-, 3 : 5-*di-iodo*-, and 3 : 5-*dinitro-salicylic chlorides*, melting at 79°, 87°, 67—68°, and 69—70° respectively; 5 : 3-*chloronitrosalicylic chloride* is liquid, and 5 : 3-*bromonitro*-, and 3 : 5-*bromonitro-salicylic chlorides* melt at 56·5° and 51° respectively. *Hydroxyuvitic dichloride* melts at 67—68°, and *α-hydroxy-β-naphthoic chloride* at 82—84°; 3 : 5-*dichlorosalicylic anhydride* melts at 186—187°.

The author has previously shown that phosphorus trichloride converts salicylic acid into salicylochlorophosphine, $C_6H_4<\genfrac{}{}{0pt}{}{COO}{—O}>PCl$, and it is now found that a substituent in the ortho-position with regard to the hydroxy-group affords no protection to the latter; *orthomethylsalicylochlorophosphine*, $C_6H_3Me<\genfrac{}{}{0pt}{}{COO}{—O}>PCl$, is obtained by the action of phosphorus trichloride on orthomethylsalicylic acid, and melts at 36—37°. M. O. F.

Action of Ethylic Cyanoacetate and of Benzylic Cyanide on Aldehydes, Ketones, and Aldehyde-Ammonia. By FR. RIEDEL (*J. pr. Chem.*, 1896, [2], **54**, 533—555. Compare Carrick, Abstr., 1892, 1086; Bechert, Abstr., 1894, i, 488; and Frost, Abstr., 1889, 597).—*Ethylic parahydroxy-α-cyanocinnamate*, $OH\cdot C_6H_4\cdot CH:C(CN)\cdot COOEt$, is readily obtained by the action of small quantities of sodium ethoxide on a solution of parahydroxybenzaldehyde and ethylic cyanoacetate in absolute alcohol. It separates from its alcoholic solution in yellow crystals, melts at 162—163°, and is readily soluble in all organic solvents, with the exception of light petroleum. On boiling with acetic anhydride, it is converted into its *acetyl* derivative, $OAc\cdot C_6H_4\cdot CH:C(CN)\cdot COOEt$, which crystallises in colourless, glistening plates, and melts at 87·5°. A chloroform solution of bromine readily reacts with ethylic parahydroxy-α-cyanocinnamate, even in the cold, to form a *compound*, $C_{19}H_{16}N_2BrO_3$, which melts at 183°. The action of bromine in the cold on the acetyl derivative is also complex, hydrogen bromide being

evolved. Sodium ethoxide hydrolyses the ethylic salt to *sodium-α-paradihydroxybenzylmalonate*, which, on treatment with hydrochloric acid, yields the *free acid*, $OH\cdot C_6H_4\cdot CH(OH)\cdot CH(COOH)_2$, melting at 232°.

Ethylic orthonitro-α-cyanocinnamate, $NO_2\cdot C_6H_4\cdot CH:C(CN)\cdot COOEt$, crystallises from absolute alcohol in glistening plates, melts at 96°, and is readily soluble in most organic solvents with the exception of light petroleum. It is not acted on by bromine in the cold. The ethylic salt can best be hydrolysed by dissolving it in alcohol, precipitating by hot water and adding sodium hydroxide in small portions at a time; before the addition of fresh soda, it is necessary to wait until the alkaline reaction disappears, and also to keep the temperature below 70°. The *acid* thus obtained melts at 223°.

Ethylic metanitro-α-cyanocinnamate melts at 127—128°, and the corresponding acid at 172°.

Methylenediphenylacetamide, $CH_2(NH\cdot CO\cdot CH_2Ph)_2$, is readily obtained when hydrogen chloride is passed through a mixture of benzylic cyanide and methylal. The same compound has already been obtained by Hepp (Abstr., 1878, 66).

Benzylic cyanide and deoxybenzoin act on one another in the presence of a small quantity of sodium ethoxide dissolved in alcohol, forming the compound $CN\cdot CPh:CPh\cdot CH_2Ph$ [*αβγ-triphenylcrotonitrile*], which, after recrystallisation from a mixture of alcohol and acetic acid, melts at 212°.

Ethylic cyanoacetate also reacts with deoxybenzoin under similar conditions, with formation of a compound, $COOEt\cdot C(CN):CPh\cdot CH_2Ph$ [*ethylic α-cyano-βγ-diphenylcrotonate*], which melts at 163°.

Although ethylic cyanoacetate does not form condensation products with acetaldehyde itself, it reacts with aldehyde-ammonia either alone or, still better, in alcoholic solution. The product, $C_7H_{10}N_2O_2$, is insoluble in all organic solvents, and is best recrystallised from boiling water; on prolonged boiling, however, with water, paraldehyde is formed. The compound has no definite melting point, as it decomposes on heating. Dilute alkalis and acids decompose it, yielding ammonia; alcoholic ammonia also reacts with the substance under pressure, yielding a compound $C_6H_9N_2O$.

Diacetonitrile also reacts with aldehyde-ammonia, yielding small quantities of a compound $C_4H_9N_2O$ (?), the constitution of which could not be determined.

Cyanacetic and malonic acids, ethylic malonate, and ethylic acetoacetate, all react with aldehyde-ammonia; the products thus formed are white, crystalline compounds, which could not be closely investigated, on account of the readiness with which they decompose. J. J. S.

Basic Coumarins. By Hans von Pechmann (*Ber.*, 1897, **30**, 277—278).—The synthesis of coumarins from ethylic acetoacetate and phenols is applicable to amidophenols, which give rise to amidocoumarins and their derivatives.

Dimethylamido-β-methylcoumarin, $NMe_2\cdot C_6H_3{<}\begin{matrix}O\text{——}CO\\ CMe:CH\end{matrix}$, obtained from ethylic acetoacetate and dimethylmetamidophenol, crystallises from alcohol in yellowish needles, exhibiting greenish fluorescence; it melts at 143°, and effloresces in dry air, becoming colourless.

The solutions in alcohol and ether exhibit violet fluorescence, and the salts of mineral acids have a copper-red fluorescence.

M. O. F.

Flavone Derivatives, IV. By J. BRÜLL and PAUL FRIEDLAENDER (*Ber.*, 1897, **30**, 297—302. Compare Abstr., 1896, i, 607).—Diacetylresacetophenone is best prepared by heating resacetophenone with acetic anhydride and sodium acetate for a short time, and pouring the mass into water. On bromination, it yields derivatives containing bromine in the nucleus, as well as an oily product containing bromine in the side chain; the latter is converted by alkalis into metahydroxyketocoumaran, $OH\cdot C_6H_3<{O \atop CO}>CH_2$, which has previously been described. The *acetate* crystallises in long needles, and melts at 80·5°. Hydroxyketocoumaran readily reacts with aldehydes, yielding products identical with those obtained by the action of aldehydes on the oily bromination product of diacetylresacetophenone. *Trihydroxyflavone*, $C_6H_3(OH)_2\cdot C \ll {O—C_6H_3\cdot OH \atop CH\cdot CO}$, is obtained by condensation with protocatechuic aldehyde, and crystallises in slender, bright yellow needles. The alkaline solution is reddish-violet, whilst the solution in sulphuric acid is orange red. The *triacetate*, which crystallises in colourless needles melting at 168°, dyes orange-yellow shades on alumina, and brown on iron or chromium mordants. The *dihydroxyflavone* obtained from metahydroxybenzaldehyde crystallises in yellow needles decomposing at about 240°, and forms yellow solutions in sulphuric acid and in aqueous soda. Acetylpeonol, on bromination, yields a *monobromopeonol*, $OMe\cdot C_6H_2Br(OH)\cdot CO\cdot CH_3$, which crystallises in long, white needles melting at 171°. It is accompanied by the monobromacetylpeonol, $OMe\cdot C_6H_3(OAc)\cdot CO\cdot CH_2Br$, which has been previously described. The further action of bromine on monobromopeonol yields a mixture of derivatives which has not been carefully examined.

Monobromacetylpeonol reacts with benzaldehyde to form *metamethoxyflavone*, $C_{16}H_{12}O_3$, which crystallises in plates, and melts at 143·5°. It was found impossible to prepare a methoxyketocoumaran by the action of alkalis on the bromide. The *compound* with piperonal forms lustrous, yellow plates melting at 175°, and gives an eosin-red coloration with sulphuric acid. The *compound* with furfuraldehyde crystallises in yellowish needles melting at 136°.

A. H.

A Dye derived from Dibromogallic Acid. By ALEXANDRE BIÉTRIX (*Bull. Soc. Chim.*, 1896, [4], **15**, 235—236).—The author has examined the brown substance formed by the oxidation of an alkaline solution of dibromogallic acid when it is exposed to the air. He finds that a bromide and carbonate are formed, and at the same time a salt of an organic acid, which is precipitated on adding hydrochloric acid. The acid is insoluble in all organic solvents, is violently attacked by nitric acid with formation of oxalic acid, but does not react with acetic chloride or acetic anhydride. The barium salt has, from analysis, the composition $C_{12}H_8Ba$.

The dye is of little use from a practical point of view. M. W. T.

Dinitrodiphenylethylenedisulphone. By HEINRICH LIMPRICHT [and PAROW] (*Annalen*, 1896, **294**, 243—252. Compare Abstr., 1894, i, 292).—*Dinitrodiphenylethylenedisulphone*, $C_2H_4(SO_2\cdot C_6H_4\cdot NO_2)_2$, is obtained by the action of ethylenic bromide (1 mol.) on sodium metanitrobenzenesulphinate (compare *loc. cit.*); it crystallises in white needles, melts at 226°, and is scarcely soluble in boiling organic solvents. *Diamidodiphenylethylenedisulphone*, $C_2H_4(SO_2\cdot C_6H_4\cdot NH_2)_2$, dissolves sparingly in boiling alcohol, and melts at 245°; the *hydrochloride* blackens at 275°, and effervesces at 295°. The *sulphate* crystallises in slender needles, and on adding sodium nitrite to the solution, and then treating it with copper powder, a *compound* is obtained which melts at 266°, and probably has the constitution $C_2H_4(SO_2\cdot C_6H_4\cdot OH)_2$.

Nitrophenylsulphone-ethylic alcohol, $NO_2\cdot C_6H_4\cdot SO_2\cdot CH_2\cdot CH_2\cdot OH$, is prepared by treating ethylenedinitrophenyldisulphone with boiling, aqueous alkali (1 mol.), and crystallises from ether in large, colourless prisms melting at 78·5°; the *methylic* and *ethylic* ethers melt at 72° and 93° respectively. If excess of alkali is employed in preparing this substance, a *compound* is formed which crystallises from alcohol in yellow needles and melts at 133°; it probably has the constitution $O(C_2H_4\cdot SO_2\cdot C_6H_4\cdot NO_2)_2$.

Amidophenylsulphone-ethylic alcohol, $NH_2\cdot C_6H_4\cdot SO_2\cdot CH_2\cdot CH_2\cdot OH$, is obtained by the action of alkali on diamidodiphenylethylenedisulphone, and by reducing nitrophenylsulphone-ethylic alcohol; the *hydrochloride* crystallises in prisms, and melts at 210°, and the *platinochloride* crystallises in small, yellow prisms.

Nitrophenylsulphone-acetic acid, $NO_2\cdot C_6H_4\cdot SO_2\cdot CH_2\cdot COOH$, is prepared by oxidising the alcohol with potassium permanganate or potassium dichromate, and crystallises from ether in white needles melting at 57°; the *potassium* and *silver* salts form white needles.

Dinitrodiphenyldisulphonediethylamine, $NH(C_2H_4\cdot SO_2\cdot C_6H_4\cdot NO_2)_2$, arises from dinitrodiphenylethylenedisulphone under the influence of moderately concentrated ammonia at 110°, and crystallises in slender needles melting at 125°; the *nitrate* forms leaflets and prisms, and melts at 205°, and the *hydrochloride* crystallises in slender, white needles, melting at 204°.

Diamidodiphenyldisulphonediethylamine, $NH(C_2H_4\cdot SO_2\cdot C_6H_4\cdot NH_2)_2$, is obtained from the foregoing compound on reduction with stannous chloride; the *hydrochloride* forms yellowish prisms, darkens at 230°, and melts at 235°. M. O. F.

Action of Diazo-compounds on Benzenesulphinic Acid. By ARTHUR R. HANTZSCH and MARTIN SINGER (*Ber.*, 1897, **30**, 312—319).—The authors have prepared a large number of diazosulphones by the action of diazo-compounds on benzenesulphinic acid, in the hope of obtaining further instances of stereoisomerism in the diazo-derivatives; the diazosulphones obtained, however, appear to be, without exception, *anti*-compounds, analogous to the *anti*-diazosulphonates, the corresponding *syn*-derivatives seeming incapable of existence.

Paratoluenediazophenylsulphone, $C_6H_4Me\cdot N_2\cdot SO_2Ph$, from diazoparatoluidine and benzenesulphinic acid, crystallises from alcohol in slender, yellow needles decomposing at 90°.

Orthoanisoildiazophenylsulphone, $OMe\cdot C_6H_4\cdot N_2\cdot SO_2Ph$, prepared from orthanisidine, crystallises from alcohol in golden needles melting at 104°, the corresponding *para*-derivative from paranisidine melts at 73—74°.

Parachlorobenzenediazophenylsulphone, $C_6H_4Cl\cdot N_2\cdot SO_2Ph$, from *para*-chlorodiazobenzene chloride, crystallises from boiling alcohol in yellow needles melting at 102—103°; this compound is also produced by the action of *syn*-chlorobenzenediazocyanide on benzenesulphinic acid, the *anti*-diazocyanide also producing the same compound.

Parabromobenzenediazophenylsulphone forms yellowish-red needles melting at 116°. It is reduced by zinc dust in glacial acetic acid solution to parabromophenylsulphazide melting at 162°.

Tribromobenzenediazophenylsulphone [$Br_3 : N_2SO_2Ph = 2:4:6:1$], from tribromodiazobenzenesulphate, decomposes at 122°.

a-Naphthalenediazophenylsulphone, $C_{10}H_7\cdot N_2\cdot SO_2Ph$, is obtained in golden plates melting at 95°; the corresponding β-derivative cannot be obtained in a pure state.

Paradiazobenzoic acid phenylsulphone, $COOH\cdot C_6H_4\cdot N_2\cdot SO_2Ph$, from the chloride of paradiazobenzoic acid, crystallises from hot alcohol in garnet-red needles, decomposing at 122—123°. The corresponding compound, produced by the condensation of orthodiazobenzoic acid with benzenesulphinic acid, is quite different; it crystallises from hot glacial acetic acid in white prisms melting at 169—170°, is insoluble in alkali carbonates, very stable towards ammonia and alkali hydroxides, and, lastly, it combines with β-naphthol. From these considerations, it seems probable that, whilst the para-compound is the true carboxylic acid of the diazosulphone, the compound derived from orthodiazobenzoic acid is either, I, an inner diazonium salt, or, II, an inner *syn*-diazoanhydride, formed by the benzenesulphinic acid attaching itself to the carbonyl group of the diazoanthranilic acid.

I. $N\vdots N<\genfrac{}{}{0pt}{}{C_6H_4}{\text{———}O}>C(OH)\cdot SO_2Ph$ II. $N\ll\genfrac{}{}{0pt}{}{C_6H_4}{N\cdot O}>C(OH)\cdot SO_2Ph.$

On heating the compound with water in a closed tube at 120—230°, salicylic acid is produced. J. F. T.

Orthotoluenesulphinic Acid. By JULIUS TROEGER and WALTHER VOIGTLÄNDER-TETZNER (*J. pr. Chem.*, 1896, [2], 54, 513—532).—Sodium orthotoluenesulphinate, $C_7H_7SO_2Na + 4H_2O$, is easily prepared from the product formed by the action of a mixture of zinc dust and water on orthotoluenesulphochloride by treating it with sodium carbonate. It is most conveniently purified by converting it into the free acid and again neutralising with sodium carbonate. It is difficult to obtain this salt in well-developed crystals, as it is so very soluble both in water and in 95 per cent. alcohol, although insoluble in absolute alcohol and ether. The *barium* salt, $(C_7H_7SO_2)_2Ba + 3H_2O$, and the *strontium* and *calcium* salts, which also crystallise with $3H_2O$, are described. The acid itself (compare Limpricht, Abstr., 1887, 723) is extremely soluble in water, and melts at 80°. On boiling with water for about 3 hours, the sulphinic acid is converted into *orthotoluic disulphoxide*, $(C_7H_7)_2S_2O_2$, which separates as an oil, and orthotoluenesulphonic acid, which re-

mains in solution. The disulphoxide separates from its alcoholic solution in glistening crystals, and melts at 95—96°. It is insoluble in water, but readily soluble in alcohol or ether. A similar decomposition occurs when the sulphinic acid is neutralised with sodium carbonate unless care is taken to keep the mixture cool. The disulphoxide, on treatment with zinc dust, yields zinc toluenesulphinate and the zinc derivative of tolylic hydrosulphide; and on warming it with potash (1 : 2), it yields *orthotolylic bisulphide*, which crystallises from its alcoholic solution in yellowish plates melting at 38°; the byeproducts consist of orthothiocresol and potassium orthotoluenesulphinate. On reduction in the cold with zinc and hydrochloric acid, sodium orthotoluenesulphinate is converted into orthotolylic bisulphide and orthothiocresol; if, however, the mixture is not kept cool, the sulphonic acid and disulphoxide are obtained. If hydrogen sulphide is passed through a methyl alcoholic solution of the sulphinic acid for 40 hours, *orthotolylic pentasulphide*, $(C_7H_7)_2S_5$, and *orthotolylic tetrasulphide*, $(C_7H_7)_2S_4$, are formed. Both these compounds are oils, but whilst the pentasulphide separates during the reaction, the tetrasulphide remains dissolved in the alcohol. Chlorine converts sodium orthotoluenesulphinate into orthotoluenesulphochloride, and bromine into *orthotoluenesulphobromide* (m. p. 90°).

The following alkylsulphones, $C_7H_7SO_2R$, have been obtained by the action of alkylic iodides on sodium orthotoluenesulphinate: *Methyl-*, *ethyl-*, *normal* and *iso-propyl-*, *normal* and *iso-butyl-*; *normal amyl-*, *β-hexyl-*, and *benzyl-orthotolylsulphones*, all of which are oily substances. *Orthotolylcetylsulphone*, $C_7H_7\cdot SO_2\cdot C_{16}H_{33}$, crystallises in needles and melts at 65°. These monosulphones cannot be hydrolysed, and are not acted on by reducing agents.

Diorthotolylethylenedisulphone, $C_2H_4(SO_2\cdot C_7H_7)_2$, obtained by warming an alcoholic solution of the sodium sulphinate with ethylenic dibromide for 20 hours on the water bath, melts at 94—95°. It is not readily reduced, but can be hydrolysed by 33 per cent. potassium hydroxide solution, yielding *orthotolylsulphonethylic alcohol*, $C_7H_7\cdot SO_2\cdot CH_2\cdot CH_2\cdot OH$, and potassium orthotoluenesulphinate.

Diorthotolylpropylenedisulphone, $C_7H_7\cdot SO_2\cdot CHMe\cdot CH_2\cdot SO_2\cdot C_7H_7$, *diorthotolyltrimethylenedisulphone*, $C_7H_7\cdot SO_2\cdot (CH_2)_3\cdot SO_2\cdot C_7H_7$, *triorthotolylpropenyltrisulphone*, $C_3H_5(SO_2\cdot C_7H_7)_3$, and *orthotolylallylsulphone*, $C_3H_5\cdot SO_2\cdot C_7H_7$, are all oily substances; the compound last mentioned combines with bromine, forming an oily *dibromide*, whilst at 150°, with hydrogen bromide, it yields *orthotolylbromopropylsulphone*,

$$CH_3\cdot CHBr\cdot CH_2\cdot SO_2\cdot C_7H_7,$$

which is also an oil.

Orthotolylsulphonacetone, $C_7H_7\cdot SO_2\cdot CH_2\cdot COMe$, obtained by the action of monochloracetone on sodium orthotolylsulphinate, is an oil, and yields an oily *oxime* and *hydrazone*. J. J. S.

Cœrulignone Colouring Matters. By CARL T. LIEBERMANN and JULIAN FLATAU (*Ber.*, 1897, 30, 234—242).—Cœrulignone,

$$\begin{array}{l} C_6H_2(OMe)_2\cdot O \\ | \qquad\qquad\quad\;\; | \\ C_6H_2(OMe)_2\cdot O \end{array}$$

combines with primary aromatic bases, forming beautiful, blue colouring matters, in accordance with the equation,

$$C_{16}H_{16}O_6 + 2NH_2X = 2CH_3{\cdot}OH + C_{14}H_{12}O_4(NX)_2\ ;$$

this change is generally applicable to aromatic primary amines which are not readily oxidised, but secondary and tertiary bases are indifferent towards cœrulignone. The colour bases produced in this manner probably have the constitution expressed by one of the formulæ, $\begin{matrix} O{:}C_6H_3(OMe){\cdot}NX \\ | \qquad\qquad\quad | \\ O{:}C_6H_3(OMe){\cdot}NX \end{matrix}$ and $\begin{matrix} NX{:}C_6H_3(OMe){\cdot}O \\ | \qquad\qquad\quad | \\ NH{:}C_6H_3(OMe){\cdot}O \end{matrix}$; they are easily reduced to leuco-compounds by treatment with sulphurous acid.

Dianilidodimethoxydiphenylquinone (*lignone-blue*), $C_{14}H_{12}O_4(NPh)_2$, is obtained on adding aniline to cœrulignone with hot acetic acid; it crystallises from chloroform in lustrous needles containing the solvent, which, however, is removed on heating at 110°, the crystals losing their lustre. *Paratoluidodimethoxydiphenylquinone* (*paradimethyl-lignone blue*), $C_{14}H_{12}O_4(N{\cdot}C_6H_4Me)_2$, crystallises from the blue, chloroform solution in needles having a metallic lustre; the spectrum of the solution exhibits two bands near the D line.

Hexamethyl-lignone-blue, *paradibromolignone-blue*, *metadichlorolignone-blue*, *orthodimethoxylignone-blue*, *lignone-blue-orthodicarboxylic acid*, and *lignone-blue-metadicarboxylic acid*, have been also prepared; *sodium lignone-blue-paradisulphonate* is obtained from cœrulignone, acetic acid, and sodium sulphanilate. M. O. F.

Reactions distinctive of the Rosanilines and of Carbinols containing Amido-groups. By AUGUSTE ROSENSTIEHL (*Bull. Soc. Chim.*, 1896, [3], **15**, 327—330).—The author criticises the work of Prud'homme on the constitution of 'patent blue' (Abstr., 1896, i, 735). This substance, although it had never been isolated, or analysed by Prud'homme, judging from its reactions, has the formula of a carbinol derivative. The formation of a benzidine derivative when it is oxidised by lead peroxide, and the permanency of the colour in the presence of alkalis, supposed by Prud'homme to be characteristic of a carbinol, are shown by the author to be equally characteristic of the rosanilines.

M. W. T.

Quinoidal Derivatives of Phenolphthalein. By RUDOLF NIETZKI and EDUARD BURCKHARDT. (*Ber.*, 1897, **30**, 175—180).—Herzig's ethylic salt of phenolphthalin does not, like the corresponding fluorescein derivative, yield a quinoidal ethylic salt on oxidation; the tetrabromo-derivative, however, does so readily.

The *ethylic* salt of *tetrabromophenolphthalin*, produced by the action of bromine on a solution of the ethylic salt of phenolphthalin in glacial acetic acid solution, crystallises from this solvent in colourless needles melting at 163°; on treatment with acetic anhydride, it yields a *diacetyl* derivative melting at 231°. When pure, its solution in alkali is colourless, but on oxidation with potassium ferricyanide, a blue precipitate is obtained, which is the potassium salt of the *quinoidal ethylic* salt of *tetrabromophenolphthalin*. The free *ethylic salt*,

$$O{:}C_6H_2Br_2{:}C(C_6H_2Br_2{\cdot}OH){\cdot}C_6H_4{\cdot}COOEt,$$

is best produced by dissolving the potassium salt in water, and covering

the solution with benzene; on cautiously acidifying with acetic acid and shaking the mixture while in the water bath, the ethylic salt is dissolved by the benzene, and separates out on cooling in yellow needles containing benzene of crystallisation. The compound crystallises from alcohol in blood-red prisms melting at 210—215°, and is a powerful dye, colouring wool and silk a nearly pure blue. It is a remarkable instance in favour of the chemical theory of dyeing; for a carefully acidified solution of its alkali salt, although nearly colourless, dyes a piece of silk or wool immersed in it an intense blue.

By the double decomposition of the potassium salt with silver nitrate and the action of ethylic iodide on the silver salt thus obtained, the *diethylic salt*, $O{:}C_6H_2Br_2{:}C(C_6H_2Br_2{\cdot}OEt){\cdot}C_6H_4{\cdot}COOEt$, is produced; this crystallises from light petroleum in sulphur-yellow needles melting at 150—151°. On partial hydrolysis with dilute sulphuric acid, this salt yields the *monethylic* ether, $O{:}C_6H_2Br_2{:}C(C_6H_2Br_2{\cdot}OEt){\cdot}C_6H_4{\cdot}COOH$, in colourless needles melting at 237°. That the ethylic group in this compound is attached to the hydroxyl and not to the carboxyl, group is shown from the fact that it readily yields an *acetyl* compound, which crystallises from glacial acetic acid in colourless needles melting at 110—111°.

None of the preceding substances are produced by ethylation of tetrabromophenolphthalein by means of ethylic bromide, the only substance formed being a colourless *diethylic* salt melting at 175°, which is, without doubt, the lactone compound $CO{<}{\substack{C_6H_4\\O\text{——}}}{>}C(C_6H_2Br_2{\cdot}OEt)_2$.

J. F. T.

A New Yellow Dye derived from Dinitrofluorescein. By FRÉDÉRIC REVERDIN (*Ber.*, 1897, **30**, 332—334).—By the action of ammonia at the ordinary temperature on dinitrofluorescein, a yellow dye is produced which dyes wool from an acid bath a yellow resembling that of tartrazine. The compound is probably an imido-derivative, formed by the replacement of the oxygen atom of the dinitrofluorescein by an imide group.

Other nitro-derivatives of fluorescein behave similarly. J. F. T.

β-Napthyl Propyl Ketone. By G. PERRIER (*Bull. Soc. Chim.*, 1896, [3], **15**, 322—323. Compare Rousset, this vol., i, 75).—By the action of aluminium on a boiling solution of naphthalene and butyric chloride in carbon bisulphide, the author obtains the compound

$$Al_2Cl_6,2C_3H_7{\cdot}CO{\cdot}C_{10}H_7.$$

It is a crystalline substance melting at 92—95°, decomposing about 97°, very soluble in chloroform and carbon bisulphide, and slightly so in light petroleum. Absolute alcohol and water decompose it with formation of β-naphthyl propyl ketone. The author has also obtained two benzoylanthracenes, two *benzoylphenanthrenes*, a *benzoylacenaphthene*, a *benzoylfluorene*, a *butyryldiphenyl*, a *benzoylretene*, and certain acetophenolenes.

M. W. T.

Action of Nitrous Acid on 2:3′-Naphtholsulphonic Acid. By RUDOLF NIETZKI and TH. KNAPP (*Ber.*, 1897, **30**, 187—190).—A substance which forms red crystals with a golden lustre is often formed by the action of nitrous acid on Schaeffer's β-naphtholsulphonic acid; this compound is best prepared by the action of fuming nitric acid

on the sulphonic acid at a low temperature, when it is obtained as a brittle mass, with a beetle-green lustre. It has the formula

$$C_{20}H_{13}NS_2O_8 + H_2O$$

and is probably an indophenol derived from β-naphthaquinone,

$$SO_3H\cdot C_{10}H_5O{:}N\cdot C_{10}H_5(OH)\cdot SO_3H\ [N:O:SO_3H = 1:2:3' \text{ and } N:OH:SO_3H = 1:2:3'].$$

It gives red solutions with acids and yellow with alkalis, but in both cases the colours soon change. Reducing agents convert it into a colourless compound, from which, however, the original substance cannot be recovered by oxidation. When heated with aniline, it yields a *compound*, $NPh{:}C_{10}H_5(SO_3H){:}N\cdot C_{10}H_5(SO_3H)\cdot NHPh$, which crystallises in small, yellowish-brown needles containing $1H_2O$. A. H.

Ethereal Oil of Bucco Leaves. By IWAN L. KONDAKOFF [with BIALOBRZESKI] (*J. pr. Chem.*, 1896, [2], **54**, 433—442. Compare Shimoyama, Abstr., 1888, 1205).—From this oil, the following substances were isolated. (1) A stearoptene, $C_{10}H_{16}O$, of phenol-aldehydic character, already described, and named diosphenol. This melts at 82°, and boils at 112° under 14 mm. pressure, and at 232° under 755 mm., but it undergoes partial decomposition at the latter temperature; it has a faint odour, resembling that of thymol. It restores the colour to magenta that has been decolorised with sulphurous acid, gives a silver-mirror with ammoniacal silver solution, yields a *phenylhydrazone* which can be obtained at a low temperature in yellowish crystals, readily deliquescing at the ordinary temperature, and an *oxime*, $OH\cdot C_9H_{14}\cdot CH{:}NOH$, which crystallises in groups of six-sided plates, and melts at 156°. Moist silver oxide oxidises it to an acid which does not crystallise and forms amorphous salts. This constituent of the oil was separated by cooling it to $-20°$. It was found possible to separate the residual oil, the so-called elæoptene, into two constituents. (2) One of these is a substance, $C_{10}H_{18}O$, with the properties of a hydroaromatic ketone, and closely resembling menthone. It boils at 207—209° under 757 mm. pressure, and at 97—99° under 20 mm. It has a sp. gr. = 0·9145 at 0°/0°, and 0·8994 at 18·5°/18·5°; its specific rotation is $\alpha_D = -6·12°$. It yields an *oxime*, $C_{10}H_{18}{:}NOH$, which boils at 140—143° under 20 mm. pressure, at 130—133° under 12 mm., has a sp. gr. = 0·9763 at 0°/0°, and 0·9627 at 18·5°/18·5°; its specific rotation is $\alpha_D = +12·7°$. With bromine, it yields a liquid compound, $C_{10}H_{17}BrO,Br_2$, which decomposes spontaneously with evolution of hydrogen bromide. (3) The second constituent of the elæoptene is a hydro-aromatic hydrocarbon, $C_{10}H_{18}$; this boils at 174—176° under 762 mm. pressure, at 65—67° under 14 mm., has a sp. gr. = 0·8802 at 0°/0°, and 0·8648 at 18·5°/18·5°; its specific rotation is $\alpha_D = +60·20°$. It has an odour resembling that of peppermint; it decolorises 1 per cent. permanganate, and reacts vigorously with bromine. C. F. B.

A Partial Synthesis of Camphor. By ALBIN HALLER (*Bull. Soc. Chim.*, 1896, [3], **15**, 324—327).—The author claims priority over the work of Bredt and Rosenberg (Abstr., 1896, i, 178). M. W. T.

Xanthorrhœa Resins. By K. HILDEBRAND (*Arch. Pharm.*, 1896, **234**, 698—707. Compare Abstr., 1894, i, 47).—Yellow xanthorrhœa resin contains 4 per cent. of free paracoumaric acid, 0·5 of free cinnamic

acid, 7 per cent. of paracoumaric acid, and 0·6 per cent. of cinnamic acid combined with tannol, also 1 per cent. of styracin and phenylpropylic cinnamate (?), 0·6 per cent. of parahydroxybenzaldehyde and vanillin, and 80 per cent. of xanthoresinotannol, chiefly in the form of its paracoumarate. The red resin contains no trace of cinnamic acid, but 1 per cent. of free coumaric acid, 2 per cent. of the same acid combined with tannol, 0·6 per cent. of parahydroxybenzaldehyde, and 85 per cent. of erythroresinotannol chiefly as its paracoumarate. *Xanthoresinotannol* $C_{43}H_{45}O_9 \cdot OH$, is insoluble in ether, benzene, chloroform, and carbon bisulphide, but readily soluble in alcohol, acetic acid, ethylic acetate, potash, acetone, and phenol. Its *benzoyl* and *acetyl* derivatives were prepared. On distillation with zinc dust, it gave benzene, toluene, phenol, and naphthalene; and on oxidation with nitric acid it yielded picric acid. On treatment with sodium peroxide, it gave a small quantity of paracoumaric acid.

Erythroresinotannol, $C_{40}H_{39}O_9 \cdot OH$, also yielded an *acetyl* and a *benzoyl* derivative. On oxidation with nitric acid, it gave picric acid, and on distillation with zinc dust, benzene, and phenol.

J. J. S.

Convolvulin, the Glucoside of Tubera Jalapæ. (Ipomæa Purga Hayne.) By M. HOEHNEL (*Arch. Pharm.*, 1896, **234**, 647—685). —Convolvulin, $C_{54}H_{96}O_{27}$, obtained from *Tubera Jalapæ* by Mayer's method, after purification by repeated solution in alcohol and precipitation with ether, is a pure white, amorphous substance, insoluble in ether, benzene, and water, only sparingly soluble in chloroform, but readily so in alcohol, glacial acetic acid, and ethylic acetate. It melts at 150—155° and readily reduces ammoniacal silver nitrate, but acts slowly with Fehling's solution unless previously hydrolysed. *Tribromoconvolvulin*, $C_{54}H_{93}Br_3O_{27}$, obtained by the action of bromine on an ice-cold solution of convolvulin in acetic acid, is also a white, amorphous powder. It is readily soluble in ether and decomposes on keeping. *Tribenzoylconvolvulin*, which is a white, amorphous substance melting at 125—131°, is readily soluble in alcohol and ether, but insoluble in light petroleum. When acetylated by Liebermann's method (*Ber.*, 1878, **11**, 1169) convolvulin yields a *nonacetyl* derivative, $C_{54}H_{87}Ac_9O_{27}$, which could not be obtained in a crystalline form; it is readily soluble in most organic solvents, and melts at 112—115°.

On hydrolysis with barium hydroxide (compare Abstr., 1894, i, 540), the glucoside yields the three acids, methylethylacetic acid, which is volatile with steam, and purgic and convolvulic acids, which are not. *Purgic acid*, $C_{25}H_{46}O_{12}$, is readily soluble in ether, and can thus be separated from convolvulic acid. From 200 grams of convolvulin, the author obtained 25 grams of purgic and 125 grams of convolvulic acid. Purgic acid is a yellowish, hygroscopic substance which is readily soluble in water, alcohol, and ether. It does not reduce Fehling's solution unless previously hydrolysed. Its *barium* salt, $C_{25}H_{44}BaO_{12}$ is an amorphous, hygroscopic powder which is readily soluble in water. *Tribenzoylpurgic acid*, obtained by the Baumann-Schotten method, is a white, amorphous powder readily soluble in alcohol and ether. To convolvulic acid (compare Kromer, Abstr., 1894, i, 540), the author gives

the formula $C_{45}H_{80}O_{28}$; it melts at 150—155° and has a sp. rotatory power $[\alpha]_D = -34° 68'$. Its *barium* salt $(C_{45}H_{79}O_{28})_2Ba + 2H_2O$, *calcium* salt, $(C_{45}H_{79}O_{28})_2Ca$, *tetrabenzoyl* derivative, which melts at 115—118°, and *octacetyl* derivative were all prepared.

Purgic acid is slowly hydrolysed by mineral acids or more quickly by superheated steam, the products being an uncrystallisable sugar, a volatile acid, namely, *decenoic acid*, $C_9H_{17}{\cdot}COOH$, and a non-volatile acid, *hydroxylauric acid*, $OH{\cdot}C_{11}H_{22}{\cdot}COOH$. The *silver* and *calcium* salts of the decenoic acid are described, but the amount of acid obtained was not sufficient to determine its actual constitution. Hydroxylauric acid crystallises in small plates, it is insoluble in water and light petroleum, but readily soluble in alcohol and ether. The *silver* salt, *copper* salt, *methylic* salt, and *monobenzoyl* derivate (m. p. 41·5°) are described.

Convolvulic acid is hydrolysed by superheated steam yielding *d*-glucose and *convolvulinolic acid*, $C_{15}H_{30}O_3$; the latter melts at 51·5° (compare Kromer). The *silver*, *barium*, and *ethylic* salts (m. p. 22·5°) are described, as also the reactions of the acid with hydrogen chloride and bromide. Convolvulinolic acid, on oxidation with potassium permanganate or with nitric acid, yields *ipomic acid*, $C_{10}H_{18}O_4$, which is isomeric with sebacic acid, also a valeric acid, probably methylethylacetic acid. (Compare also Taverne, Abstr., 1895, i, 119). J. J. S.

Curcumin. By GIACOMO L. CIAMICIAN and PAUL G. SILBER (*Ber.*, 1897, **30**, 192—195).—Curcumin, when purified by repeated crystallisation, melts at 183°, whereas Jackson and Menke (*Amer. Chem. Journ.*, **4**, 77) give it as 178°; the formula, moreover, is $C_{19}H_{14}O_4(OMe)_2$, and not $C_{14}H_{14}O_4$ as stated by previous observers. The *diacetate*, $C_{19}H_{12}O_2(OMe)_2(OAc)_2$, is prepared by the action of acetic anhydride, and crystallises in large, yellow needles melting at 170—171°. *Dimethylcurcumin*, $C_{19}H_{12}O_2(OMe)_4$, obtained by the action of methylic iodide and methyl alcoholic potash on curcumin, crystallises in golden-yellow needles, melts at 135°, and as it is insoluble in alkalis, probably contains no free hydroxyl groups. With hydroxylamine, curcumin yields a *substance* which melts at 173°, and probably has the formula $C_{21}H_{19}NO_5$; it also reacts with phenylhydrazine, but the product has not yet been obtained pure. A. H.

Synthesis of Tetrahydropyridine Derivatives, and their Conversion into Piperidine Derivatives. By ANDREAS LIPP (*Annalen*, 1896, **294**, 135—164. Compare Abstr., 1896, i, 317).—1-*Methyl*:2-*hydroxyethyl*-Δ^2-*tetrahydropyridine*, $CH_2{<}{\genfrac{}{}{0pt}{}{CH_2{\cdot}NMe}{CH_2{-}CH}}{>}C{\cdot}CH_2{\cdot}CH_2{\cdot}OH$, is obtained by cautiously adding a 40 per cent. solution of formaldehyde to methyltetrahydropicoline dissolved in water; after 24 hours, the liquid is distilled in a current of steam, the distillate saturated with hydrogen chloride, and evaporated to dryness. The base boils at 199—200° under a pressure of 710 mm., and is a colourless, mobile liquid, with a feebly ammoniacal odour; the sp. gr. = 0·96007 at 0°/0°. The *hydrochloride* and *platinochloride* melt at 155—157° and 200—205° respectively; the *aurochloride* sinters at 110°, melts at 119—121°, and decomposes at 135—140°. The *mercurichloride* separates from water in colourless, lustrous crys-

tals, and incompletely melts at 161—162°, fusion becoming complete at 195—200°; the *picrate* melts at 126—127°, and decomposes at 200°.

1-*Methylpipecolylalkine*, $CH_2<\begin{matrix}CH_2\cdot NMe\\ CH_2-CH_2\end{matrix}>CH\cdot CH_2\cdot CH_2\cdot OH$, [1-*Methyl-2-hydroxyethylpiperidine*], produced when the foregoing base is reduced with alcohol and sodium, boils at 214·5—215·5° under a pressure of 720 mm.; it is a colourless, viscous liquid resembling glycerol, and is not identical with Ladenburg's 1-methylpipecolylalkine, obtained by reducing picolylalkine and introducing a methylic group (Abstr., 1893, i, 426). The *hydrochloride* dissolves very readily in water, and separates in prismatic crystals; the *aurochloride* occurs in two modifications, melting at 72—73° and 127—128° respectively, of which the latter may be converted into the former. The *mercurichloride* melts incompletely at 166—167°, and evolves gas at 190—195°. The base combines with methylic iodide, and the *methochloride* crystallises from alcohol in needles; the *aurochloride* and *platinochloride* of the methochloride melt at 101—102° and 230—235° respectively.

1-Methyl-2-vinylpiperidine is obtained by heating 1-methylpipecolylalkine with concentrated hydrochloric acid for 2 hours at 180—185°, and is identical with the compound described by Ladenburg (*loc. cit.*); the *hydrochloride* crystallises in needles, and the platinochloride melts at 185—186°. The *aurochloride* crystallises in prisms and melts at 58—59°, and the *mercurichloride* melts at 177—178°, decomposing at 200—205°; the *picrate* crystallises in yellow prisms, and melts at 193—194°.

The author explains the discrepancy between the properties of *n*-methylpipecolylalkine prepared by his method and those of Ladenburg's compound, by bringing evidence to show that, when picolylalkine is reduced in alcoholic solution with sodium, a mixture of a primary with a secondary base is produced, owing to the ring being ruptured.

Support is given to Merling's formula for tropine. M. O. F.

Formation of Pyrazine and its Homologues from Glucose and Ammonia. By P. BRANDES and CARL STOEHR (*J. pr. Chem.*, 1896, [2], 54, 481—495).—In repetition of Tanret's experiments (Abstr., 1885, 1047), 6 parts of glucose was heated with 10 parts of 25 per cent. ammonia for 35 hours at 100°, and the product distilled with potash. From the distillate, pyridine, pyrazine, and methylpyrazine were isolated, and identified by their known properties (compare Abstr., 1895, i, 569); the last base is the main product of the reaction; its *ethiodide* crystallises in yellowish needles. A small quantity of a *dimethylpyrazine*, probably $N<\begin{matrix}CH\cdot CMe\\ CH\cdot CMe\end{matrix}>N$, was also obtained in the fraction boiling at 147—155°; it melts at 47—48°, is very volatile, and crystallises with great readiness in short, monoclinic prisms [$a:b:c = 0·7678:1:?$]. The yellow *aurochloride*, $C_6H_8N_2,HAuCl_4$, melts and decomposes at 148°, and when warmed with water yields the yellow *salt*, $C_6H_8N_2,AuCl_3$, which melts and decomposes at 144°; the *mercurichloride*, $C_6H_8N_2,6HgCl_2$, and *picrate*, $C_6H_8N_2,C_6H_3N_3O_7$, melting at 175—176°, were also prepared. Tanret's α- and β-glucosine were in reality methyl- and dimethylpyrazine respectively, in spite of the discordance between his boiling points and analyses, and those of the authors. C. F. B

Derivatives of Methylhydrazine. By WILHELM MARCKWALD and E. SEDLACZEK (*Ber.*, 1896, **29**, 2920—2927).—1 : 4-*Dimethylthiosemicarbazide*, NHMe·CS·NH·NHMe, is formed by the combination of methylthiocarbimide and methylhydrazine, and melts at 138°. 1 : 4-*Methylethylthiosemicarbazide* melts at 84°. The *platinochloride*,

$$C_4H_{11}N_3S,H_2PtCl_6,$$

forms brownish-red crystals.

4 : 1-Phenylmethylthiosemicarbazide, NHPh·CS·NH·NHMe (von Brüning, Abstr., 1890, 23), is not converted by nitrous acid into a thiocarbamide. The *hydrochloride* is very sparingly soluble in hydrochloric acid. When the carbazide is heated at 120°, hydrogen sulphide is evolved, and a mixture of methylhydrazine hydrochloride with a *triazole* derivative, $C_{15}H_{14}N_4S$, is produced; the latter is also formed when phenylmethylthiosemicarbazide is heated with phenylthiocarbimide; it melts at 175° and has basic properties, the *platinochloride* being a yellow, crystalline precipitate. Its constitution has not yet been ascertained. Phenylmethylthiosemicarbazide unites with methylic iodide to form the *hydriodide* of a new base, $C_9H_{13}N_3S,HI$, which melts at 91° and is decomposed by alkalis with formation of methylic mercaptan. The carbazide, moreover, reacts with carbonic chloride to form a *compound*, $SH\cdot C\Big\langle{NPh\cdot CO \atop N\text{——}NMe}$, which is soluble in alkalis; it melts at 163°, and then becomes changed into an isomeric compound, $SC\Big\langle{NPh\cdot CO \atop NH\text{—}NMe}$, melting at 212°.

The mercaptan readily reacts with methylic iodide to form a mixture of two hydriodides, one $C_{10}H_{11}N_3OS,HI$, melting at 120°, and the other $(C_{10}H_{11}N_3OS)_2,HI$, at 97°; the second of these is formed when the first is heated with water. These salts are decomposed by strong alkalis, with separation of methylic mercaptan. The mercaptan also reacts with iodine, but the sulphide formed has not been isolated. The isomeric compound, melting at 212°, is also soluble in alkalis, and yields a crystalline *silver salt*, $C_9H_8N_3OSAg$. It does not react with iodine, but when treated with potassium permanganate, it yields the corresponding *oxy-compound*, $CO\Big\langle{NPh\cdot CO \atop NH\text{—}NMe}$, which forms white crystals, melts at 188°, and has strongly acid properties.
A. H.

Diphenyltetrazoline. By GUIDO PELLIZZARI (*Gazzetta*, 1896, **26**, ii, 430—433).—The author has previously shown that formophenylhydrazide and formamide condense with elimination of $2H_2O$ and formation of 1-phenyltriazole (Abstr., 1895, i, 308); he now shows that, when heated alone, formophenylhydrazide condenses with itself in a similar manner, yielding *n*-diphenyltetrazoline, a compound termed by Ruhemann, who first prepared it, diphenyltetrazine (Trans., 1890, **57**, 50), and by Pinner *n*-diphenylisodihydrotetrazine. The author argues in favour of the adoption of the new name as a generic one.
W. J. P.

Sparteine. By FELIX B. AHRENS (*Ber.*, 1897, **30**, 195—200).—The oxygen atom of oxysparteine is probably present in an aldehyde

group, since oxysparteine, when heated with dilute hydrogen peroxide at 100°, is converted into an *acid*, the *barium salt* of which is a yellow, hygroscopic powder of the composition $[C_{14}H_{21}(OH)_2N_2COO]_2Ba$, and sparteine itself is converted by similar treatment into dihydroxysparteine, this acid being accompanied by trioxysparteine. The alcoholic function of the oxygen atoms of dihydroxysparteine is shown by the fact that, when heated with hydrochloric acid at 200°, it is converted into a base, $C_{15}H_{24}N_2$, identical with that obtained by the action of bleaching powder on sparteine. When oxysparteine is treated at the ordinary temperature with 3 per cent. hydrogen peroxide for a considerable time, two products are formed in addition to the acid already described. Of these, the *acid*, $C_{10}H_{16}NO_2 + 3H_2O$, separates from acetone in large, transparent crystals, melts at 287—289°, and is very hygroscopic. It forms readily soluble crystalline *ammonium*, *calcium*, and *zinc salts*, a crystalline *platinochloride* and an *aurochloride*,

$$C_{10}H_{16}NO_2,HAuCl_4,$$

which melts at 194°. The second substance was only obtained in the form of its *picrate*, $C_2H_8NO_3,C_6H_3N_3O_7$ which melts at 227—228° and decomposes at a slightly higher temperature. A. H.

Compounds of Proteid with Nucleic Acid and with Thymic Acid. By T. H. Milroy (*Zeit. physiol. Chem.*, 1896, **22**, 307—326).—The nucleins are divided into the true nucleins, which yield alloxuric bases on decomposition, and the para-nucleins, which do not. Nucleic acid and thymic acid are both precipitants of proteid matter, the precipitate consisting of artificial nuclein, in which the acid is very firmly combined. The properties (solubilities, percentage of phosphorus, behaviour towards digestive ferments) of the artificial nucleins prepared from the several proteids (syntonin, albumoses, &c.) by the use of nucleic acid are very similar to those of the true nucleins, whilst those prepared by the use of thymic acid resemble the para-nucleins; this resemblance, however, is not sufficient to establish identity.

W. D. H.

Oxidation Products of Hæmatoporphyrin and the Composition of Hæmin prepared by Different Methods. By William Küster (*Ber.*, 1897, **30**, 105—110).—Hæmatoporphyrin is formed almost quantitatively by the action of hydrogen bromide dissolved in acetic acid on hæmatin, and is converted by oxidation with chromic acid into the same products as hæmatin, the same two acids, $C_8H_{10}O_5$ and $C_8H_{10}O_6$, being formed (Abstr., 1896, i, 516).

Hæmin hydrochloride, prepared by the author according to Cloëtta's method (Abstr., 1896, i, 660), has the formula $C_{32}H_{31}ClN_4FeO_3$ ascribed to it by Nencki, whereas Cloëtta found for it the formula in which the atomic ratio of nitrogen to iron was 3 : 1. The author ascribes this difference to the action of the concentrated sulphuric acid employed by Cloëtta in its preparation. A. H.

Organic Chemistry.

Preparation of Diethylenic Hydrocarbons. By H. Fournier (*Bull. Soc. Chim.*, 1896, [iii], 15, 400—404. Compare Abstr., 1896, i, 457).—6-*Methyl*-4-*chloro*-1-*heptylene* is obtained by the action of phosphorus pentachloride on isobutylallylcarbinol; it is a colourless liquid, boiling and decomposing at 150—155°, and yields 6-methylhepta-1:3-diene when treated with alcoholic potash.

1:2:3:4-*Tetrabromo*-6-*methylheptane* is prepared by the action of bromine on a solution of the last-named hydrocarbon in chloroform; it is a viscous liquid, which does not solidify at −15°.

4-*Chloro*-1-*hexylene* is obtained by the action of phosphorus pentachloride on the corresponding alcohol; it boils and decomposes at 115—120°.

1:3-*Hexadiene* is formed by the action of alcoholic potash on the last-named product, and is a colourless liquid boiling at 72—74°, and of sp. gr. = 0·714 at 12°.

Two stereoisomeric 1:2:3:4-*tetrabromhexylenes* are obtained by treating a solution of 1:3-hexadiene in chloroform with bromine. The one is a crystalline compound melting at 91—92°, and the other a substance which remains liquid at −20°. The tetrabromide of 1:4-hexadiene, which might also be produced by removing hydrogen chloride from 4-chlorhexylene, melts at 63—64°. M. W. T.

Constitution of Isoprene. By Wladimir Ipatieff and Nicolaus von Wittorf (*J. pr. Chem.*, 1897, [ii], 55, 1—4).—Isoprene, obtained by distilling Para caoutchouc, boils at 33—38°, and, when treated with an acetic acid solution of hydrogen bromide, yields (1) a compound that is converted by aqueous potassium carbonate into dimethylethylcarbinol, and (2) β-dimethyltrimethylenic dibromide, CH_3·CMeBr·CH_2·CH_2Br, boiling at 74—75° under 16 mm. pressure (Abstr., 1896, i, 330). Of these (1) is formed in small amount only; "isoprene" thus contains a little trimethylethylene, but its main constituent, assuming it to be a chain compound (compare following abstract), must be methyldivinyl, CH_2:CMe·CH:CH_2. C. F. B.

Constitution and Synthesis of Isoprene. By Wladimir Ipatieff (*J. pr. Chem.*, 1897, [ii], 55, 4—13).—When β-dimethyltrimethylenic dibromide, made by the addition of hydrogen bromide either to isoprene (preceding abstract), or to dimethylisoallylene, is dropped into strong boiling alcoholic potash, two products are formed. One boils at 120—122°, and appears to be an *ether*, C_5H_9·OEt. The other is a hydrocarbon which boils at 32—33° and does not give the reactions of acetylene derivatives, but yet takes up 2 mols. of hydrogen bromide, regenerating the above-mentioned dibromide. It thus contains two double bonds, for the action of alcoholic potash on the dibromide is not likely to have resulted in the formation of a trimethylene ring. It differs, however, from dimethylisoallylene, which boils at 39·5—41°, and must therefore be *methyldivinyl*, CH_2:CMe·CH:CH_2, in

which the double bonds are not adjacent. In harmony with this view is the fact that, when treated with hypochlorous acid, it yields a dichlorhydrin; this melts at 81°, and has already been obtained by the addition of hypochlorous acid to isoprene (Favorsky and Mokiewsky, *Chem. Zeit.*, 1895, No. 101). This is further evidence that isoprene itself must be regarded as consisting mainly of methyldivinyl.

C. F. B.

Cyanuric Chloride. By PAUL LEMOULT (*Compt. rend.*, 1896, **123**, 1276—1278).—Cyanuric chloride was prepared by the action of chlorine on a well cooled solution of dry hydrogen cyanide in chloroform, and purified by repeated sublimation. Its vapour is readily decomposed by water vapour, and hence it must be kept in well-stoppered bottles in a carefully dried atmosphere. Its heat of combustion is 293·7 Cal. at constant volume, and 292·9 Cal. at constant pressure, its heats of formation being respectively +107·1 Cal. and +107·9 Cal. The polymerisation of three molecules of cyanic chloride to form one molecule of cyanuric chloride develops +189·05 Cal., but notwithstanding the large development of heat, the spontaneous change takes place very slowly, especially if the cyanic chloride is pure. The numbers given explain the large development of heat that accompanies the action of chlorine on hydrocyanic acid, and the considerable development of heat in the preparation of cyanuric chloride by the action of phosphorus pentachloride on cyanuric acid. It is noteworthy, however, that the substitution of hydroxyl for chlorine develops considerably less heat than in the case of phosphoryl chloride. Unlike cyanic chloride, cyanuric chloride is comparatively stable in presence of liquid water even at its boiling point.

C. H. B.

Polymerisation of some Cyanic Compounds. By PAUL LEMOULT (*Compt. rend.*, 1897, **124**, 84—86).—The values given in the preceding paper are incorrect, because in calculating the heat of formation of cyanuric chloride from its elements, account was not taken of the decomposition of the water required for the combustion of the chloride according to the equation $2C_3N_3Cl_3$ sol. + $3H_2O$ liq. + $9O = 6CO_2 + 9HCl + 3N_2$. When the correction is made, the heat of formation of cyanuric chloride becomes + 3·9 Cal. at constant volume, and + 5·2 Cal. at constant pressure. The formation of the solid chloride by the action of gaseous chlorine on liquid hydrocyanic acid develops +141·7 Cal.; by the action of phosphorus pentachloride on cyanuric acid, +12·9 Cal. The substitution of 3OH for 3Cl in cyanuric chloride develops +53·7 × 3 Cal., which is practically identical with the corresponding value for phosphoric acid. In the direct action of water on cyanuric chloride, the heat developed is +20·1 Cal. (6·7 × 3), somewhat higher than the corresponding value for acetic chloride.

The conversion of liquid cyanogen chloride into solid cyanuric chloride develops +28·7 × 3 Cal.; the conversion of dissolved cyanic acid into dissolved cyanuric acid develops +16·7 × 3 Cal., and the conversion of liquid cyanic acid into solid cyanuric acid will develop approximately +29·4 × 3 Cal. The conversion of cyanamide into melamine develops +15·5 × 3 Cal.

C. H. B.

Aluminium Ethoxide. By HOMER W. HILLYER and O. E. CROOKER (*Amer. Chem. J.*, 1897, **19**, 37—44).—Aluminium ethoxide, which was prepared by Gladstone and Tribe (Trans., 1881, 1; 1882, 5; 1886, 25) by the action of aluminium foil and iodine on alcohol, is also formed when aluminium is added to a solution of mercuric chloride in alcohol; stannic chloride gives a similar result, but the product contains aluminium chloride. The ethoxide is a pure white substance melting at 135° and boiling at 235—245° (pressure = 23 mm.).

A. H.

Purification of Phenylglucosazone. By LOUIS HUGOUNENQ (*J. Pharm.*, 1896, [vi], **4**, 447—448).—Phenylglucosazone may readily be purified by washing it in the cold with water, alcohol, and acetone sucessively and then recrystallising from anisoil. The method is preferable to that suggested by Tiemann, and yields the pure osazone melting at 204—205. J. J. S.

Preparation of Pure Starch. By OTTO N. WITT (*Bied. Centr.*, 1896, **25**, 856—857; from *Neue Zeits. Zuckerind.*, 1896, No. 11, and (with SIEMENS and HALSKE) *Ger. Pat.*, No. 88447, Class 89, July 23, 1895).—Ordinary starch is for some purposes unsuitable, as the impurities it contains yield products of decomposition some of which are coloured, others of unpleasant odour. Moreover, the cellulose covering of the grains hinders the action of chemical agents.

The following method is used for obtaining pure starch. The starch, mixed with water, is treated with potassium permanganate until the latter is no longer decolorised. The impurities are then all destroyed, whilst manganese peroxide is precipitated on to the starch grains, which are thus coloured brown. To bleach the starch, it is washed, and treated with sulphurous acid. If, however, it is desired to convert the cellulose into oxycellulose (and thus render the starch readily soluble in potash), the starch, after treatment with permanganate, is poured into dilute hydrochloric acid, and continually agitated. The chlorine which is evolved acts on the cellulose. From time to time samples are taken, washed with sulphurous acid, and their solubility in alkali tested. When the conversion into oxycellulose is complete, the starch is collected, treated with aqueous sulphurous acid, washed, and dried. The product has all the properties of pure starch. N. H. J. M.

Precipitation of Carbohydrates by Neutral Salts. By ROBERT A. YOUNG (*Proc. Physiol. Soc.*, 1896—1897, 16—18).—Crystalline carbohydrates are not precipitated by saturating their solutions with neutral salts. Glycogen is completely precipitated by saturating its solutions with magnesium sulphate, sodium magnesium sulphate, and ammonium sulphate at ordinary temperatures, and by sodium sulphate at 33°, at which temperature this salt has its maximum solubility. Starch is precipitated in a similar way. Erythrodextrin is not precipitated by such salts, and so may be readily distinguished from glycogen. Commercial dextrin gives an abundant precipitate on saturation with ammonium sulphate; this consists partly of soluble starch, partly of one or more intermediate dextrins. Achroodextrin is partly precipitated by ammonium sulphate, and inulin, partly by

magnesium sulphate. The soluble iodine compounds of the carbohydrates, including that of erythrodextrin, are precipitated by saturation with salts, often more readily than the carbohydrates themselves.

W. D. H.

A Correction [Action of Hydroxylamine on Mesityl Oxide]. By CARL D. HARRIES (*Ber.*, 1897, **30**, 460).—The compound, α-diacetonehydroxylamine, obtained by the action of alcoholic hydroxylamine on mesitylic oxide in the cold (this vol., i, 212), is only produced under exceptional experimental conditions; the compound generally formed is Naegeli's mesityloxime.

J. F. T.

Thorium. By G. URBAIN (*Bull. Soc. Chim.*, 1896, [iii], **18**, 347—349). —By treating thorium hydroxide, suspended in alcohol with acetylacetone, and subsequently concentrating the solution, the author obtains a compound of the formula $Th(C_5H_7O_2)_4$. It is a crystalline substance, melts at 171—172°, sublimes in a vacuum, is very soluble in ether and ethylenic dibromide, but only slightly so in water.

Under the same conditions, cerium hydroxide forms an insoluble, grey, amorphous substance which appears to have the composition $CeO{\cdot}CH(CO{\cdot}CH_3)_2$.

This reaction serves as a means of separating cerium from thorium.

M. W. T.

Preparation of Pure Ethylidenelactic Acid, and Preliminary Experiments on Distillation in a Vacuum. By WILHELM A. DYES (*Chem. Centr.*, 1896, i, 742—743; from *Diss.*, 1895, Heidelberg). —In the experiments on distillation, the author made use of Babo's air-pump, which he prefers on account of the small quantity of mercury required and its simple manipulation. Pure fermentation or ethylidenelactic acid is obtained by removing the water from the ordinary purchasable solution by heating at 60° under a pressure of 1 mm., and distilling the residue, at 0·5 to 1 mm. pressure, from a short-necked distilling flask immersed in a bath of Wood's metal; just before actual boiling begins, a slight liberation of water is noticed. By repeated distillation, a liquid is obtained which boils constantly at 82—85° under a pressure of 0·5 to 1 mm., and leaves scarcely any residue on evaporation. Its density at 25° is 1·23, and its composition corresponds with the formula $C_3H_6O_3$. When strongly cooled, it solidifies to a hard, white, crystalline mass, which melts at 18°, and deliquesces very rapidly in moist air. On distillation, some lactide is formed, but by performing the operation quickly and avoiding superheating, this may be reduced to a minimum. Formation of lactide occurs also on standing in warm air, or in a vacuum over sulphuric acid. A solution containing 95—96 per cent. of acid, and free from anhydride, may, however, be obtained from the commercial solution by first boiling it with water and then drying over sulphuric acid in a vacuum for a limited period. In one case, after boiling with an equal volume of water for 3 hours and drying for 107 hours, a solution containing 96·56 per cent. of acid was obtained, but on continuing the drying for 12 hours longer, the formation of anhydride was found to have reduced the strength of the solution to 96·44 per cent.

By use of the ordinary water vacuum pump, an acid of 95—99·63 per cent. may be prepared. For this purpose, the water is first driven off from a lactic acid solution of density 1·21, by heating at 100° under a pressure of 15 mm. The residue is then distilled by heating in a bath of Wood's metal at 120—121°, the receiver being kept at 90°, in order to remove any water produced by formation of anhydride in the distillate. Under a pressure of 14 mm., the product boiled at 120—121°, at 13 mm. pressure at 119—120°, at 12 mm. at 119°. The sp. gr. of a 98 per cent. acid solution at 25° was found to be 1·23, and of a 93 per cent. solution 1·228. A determination of the sp. gr. is not sufficient to indicate the content of pure acid. Although the commercial lactic acid solution does not lose acidity on standing, a 97 per cent. solution sank to 78 per cent. after remaining at a summer temperature for 6 weeks.

The following boiling points at low pressures were also observed. Lactic acid, about 85° (1 mm.); 91—92° (3 mm.). α-Hydroxyisobutyric acid, 84° (2 mm.). Mannitol, 276—280° (about 1 mm.); 285° (2·5 mm.); 290—295° (3—3·5 mm.). Dulcitol, 275—280° (about 1 mm.); 287—288° (2·5 mm.); 290—295° (3—3·5 mm.).

The following sublimation temperatures are given. Lactide, 95—96° (about 1·5 mm.); about 138° (12 mm.). Succinic acid, 160—165° (2·5—3 mm.); 156—170° (2·2 mm.). Fumaric acid, 165° (1·7 mm.). Maleic anhydride, 45—46° (2 mm.). Mesaconic acid, 139—141° (1·5 mm.); 143—145° (2 mm.). Itaconic acid, 140—141° (about 1 mm.).

E. W. W.

Researches in the Hexamethylene Series. V. The Isomerisation of Hexamethylene. By Nicolai D. Zelinsky (*Ber.*, 1897, **30**, 387—391. Compare Abstr., 1895, i, 411).—When hexamethylene iodide is heated with hydriodic acid at 230°, the hydrocarbon which is formed differs from the hexamethylene prepared by the reduction of the iodide with zinc and hydrochloric acid. The latter boils at 79—79·5° (Baeyer) 81—82° (Zelinsky), and has a sp. gr. = 0·7764 at 20°/4°. The hydrocarbon obtained by the use of hydriodic acid, on the other hand, boils at 71·5—72·5°, and has a sp. gr. = 0·7501 at 21°/4°. This substance agrees in its properties with methylpentamethylene, which, when prepared from β-methylpentamethylenic alcohol by means of hydriodic acid, boils at 71·5—72·5°, and has a sp. gr. = 0·7473 at 18°/4°. The hydrocarbon is not at once acted on by bromine, but immediately reacts with concentrated nitric acid. This reaction is not common to any of the polymethylene compounds containing a ring of six carbon atoms, but is given by methylpentamethylene and dimethylpentamethylene. The author therefore concludes that, under the influence of hydriodic acid, the hexamethylene ring is converted into a 5-carbon ring, which, under these circumstances, appears to be more stable than the 6-carbon ring. Hexahydrobenzene, which is formed by the action of hydriodic acid on benzene, also appears to be identical with methylpentamethylene.

A. H.

Parabromometadinitrotoluene and some of its Derivatives. By C. Loring Jackson and Martin H. Ittner (*Amer. Chem. J.*, 1897, **19**, 1—37. Compare Abstr., 1896, i, 214).—The object of the investigation was to study the behaviour of a bromine atom in the

ortho-position between two nitro-groups, the para-position not being occupied by a third negative group. *Parabromometadinitrotoluene* [$Me:NO_2:Br:NO_2=1:3:4:5$] is prepared from dinitrotoluidine, melting at 166°, by treating it with sodium nitrite and hydrobromic acid, the reaction requiring a long time for its completion, on account of the sparing solubility of the base and the diazo-salt in hydrobromic acid. The bromo-derivative crystallises in white prisms or irregular plates, and melts at 118°. Boiling aqueous ammonia converts it into dinitrotoluidine, and boiling aqueous soda into dinitrocresol melting at 85°. Aniline readily converts it into 4 : 3 : 5-*anilidodinitrotoluene*, $C_6H_2Me(NO_2)_2\cdot NHPh$, which crystallises in slender, orange-coloured needles, and melts at 169°; when its solution in benzene is treated with hydrochloric acid and sodium nitrite, *nitrosoanilidodinitrotoluene*, $C_6H_2Me(NO_2)_2\cdot NPh\cdot NO$, is produced quantitatively. This substance crystallises in almost colourless, rhombic plates, and melts and decomposes at 123°.

Bromodinitrotoluene does not appear to react with ethylic sodiomalonate, but gives a brilliant blue compound with sodium ethoxide; this will form the subject of a further communication.

4 : 3 : 5-*Bromodinitrobenzoic acid* is formed when bromodinitrotoluene is boiled with potassium dichromate and sulphuric acid, and in small quantity when chrysanisic acid is treated with hydrobromic acid and sodium nitrite. It crystallises in rhombic plates, is slightly soluble in water, and melts at 181°. The *sodium* salt crystallises with $4H_2O$ in slender needles and is decomposed by boiling with water or alkalis, 3 : 5 : 4-dinitrohydroxybenzoic acid (melting at 245—246°) being formed. The *silver* salt crystallises from dilute alcohol in dull, grey needles. *Ethylic bromodinitrobenzoate* crystallises in short, white needles, and melts at 105°.

4 : 3 : 5-*Anilidodinitrobenzoic acid*, which crystallises in orange-coloured needles, and melts at 239°, yields a *sodium* salt crystallising in orange-red needles with $3H_2O$. The *ethylic* salt forms bright orange-coloured prisms which melt at 154°. No nitroso-compound could be prepared.

Bromodinitrobenzoic acid readily reacts with ethylic sodiomalonate, forming *ethylic* 2 : 6 : 4-*dinitrocarboxyphenylmalonate*,

$$(COOEt)_2CH\cdot C_6H_2(NO_2)_2\cdot COOH,$$

which crystallises in thick, white prisms, and melts at 176°. Silver nitrate added to the ammonium salt produces a white precipitate of *silver ammonium* salt, which probably has the formula

$$(COOEt)_2CAg\cdot C_6H_2(NO_2)_2\cdot COONH_4.$$

Bromodinitrobenzoic acid readily forms a crystalline *salt* with 1 mol. of pyridine, and also combines with 2 mols. of pyridine to form an unstable yellow *compound* which, on repeated crystallisation, is broken up into pyridine bromide and dinitrohydroxybenzoic acid; the latter melts at 245—246°, and not at 235—237° as stated by Salkowski (*Annalen*, 1872, **163**, 36). Bromodinitrotoluene reacts with great violence with metaphenylenediamine, forming *amidophenyleneimidodinitrotoluene*, $NH_2\cdot C_6H_4\cdot NH\cdot C_6H_2Me(NO_2)_2$, which crystallises in fan-shaped groups of blunt reddish-brown prisms, and melts at 185°. No crystalline salt can be prepared, and it does not react with a second molecule of bromodinitrotoluene. *Tribromamidophenyleneimidodini-*

trotoluene, $NH_2 \cdot C_6HBr_3 \cdot NH \cdot C_6H_2Me(NO_2)_2$, obtained by the action of bromine water on the foregoing compound, crystallises in brownish-yellow, rhombic plates and melts at 22°.

Tribromanilidodinitrotoluene, $C_6H_2Br_3 \cdot NH \cdot C_6H_2Me(NO_2)_2$, is formed by the action of bromine on anilidodinitrotoluene and crystallises in yellow, rhombic plates melting at 238°. Attempts were made to prepare nitro- and anilido-derivatives of this compound in order to synthesise a substance containing a number of benzene nuclei united by nitrogen atoms, but no crystalline products could be obtained.

4 : 3 : 5-*Chlorodinitrobenzoic acid* is formed when chrysanisic acid is diazotised and the solution heated with cuprous chloride. It crystallises in well-defined prisms melting at about 159°. Bromodinitrobenzoic acid is converted by 11 per cent. aqueous hydrochloric acid at 200° into dinitrophenol [$OH : (NO_2)_2 : = 1 : 2 : 6$] and another substance, melting at 119°, probably the corresponding bromodinitrobenzene. A. H.

Action of Sulphuric Acid on Anisoil. By WILLIAM B. SHOBER (*Amer. Chem. J.*, 1896, **18**, 858—865).—The author finds that when anisoil is mixed with sulphuric acid and the mixture heated to 92°, anisoildisulphonic acid is invariably formed, the amount increasing with the proportion of sulphuric acid and with the time of heating, but it is not formed at 125° or higher temperatures.

Paranisoilsulphonic acid is always formed, the amount decreasing with increase of temperature, time of heating, and excess of sulphuric acid.

Orthoanisoilsulphonic acid is formed in largest amount when anisoil and sulphuric acid are allowed to react at ordinary temperatures It is not produced, however, if the proportion of sulphuric acid to anisoil is greater than 4 to 1. A. W. C.

Electrolysis of Quinol. By LOUIS LIEBMANN (*Chem. Centr.*, 1896, i, 804; from *Zeit. Elektrotechn. u. Elektrochem.*, 1896, 497—499).—By the electrolysis of quinol, the author has obtained a quantitative conversion into quinhydrone. A more or less concentrated, or a cold, saturated, aqueous solution of quinol is acidified with a few drops of sulphuric acid, and electrolysed under an electromotive force of 12 volts in U-tubes containing electrodes of sheet platinum or cylinders of carbon. Variations of current from 0·02 to 2 ampères do not affect the result, but the current density should be so regulated that no oxygen is given off at the anode. In about 10 minutes, the quinhydrone begins to form at the anode in long, green crystals, which after one crystallisation from alcohol are pure. If, instead of sulphuric acid, nitric acid or a nitrate is added, quinone is formed in very small quantity. The formation of quinhydrone takes place readily with an alternating current, and its production in large crystals renders it a suitable method for the demonstration of such electrolysis. E. W. W.

Phosphates of Diatomic Phenols. By HONORÉ SECRÉTANT (*Bull. Soc. Chim.*, 1896, [iii], **18**, 361—364).—The phenol is heated with excess of phosphorus pentachloride until the mixture becomes viscous; on treating the mass with cold water, a solid residue is obtained, which is purified by recrystallisation from hot water. Analysis showed that the substances had the composition $PO_4(C_6H_4 \cdot OH)_3$.

The *quinol* derivative is a white, crystalline substance, which melts

at 149° and boils at very nearly the same temperature. It is very soluble in alcohol, acetic acid, and ether, but insoluble in light petroleum, benzene, and carbon bisulphide.

The *resorcinol* derivative has similar properties, but melts at 75°.

M. W. T.

Aromatic Bisulphides. By P. GENVRESSE (*Bull. Soc. Chim.*, 1896, [iii], **15**, 409—426).—When diphenylene bisulphide is heated with strong sulphuric acid containing 60 per cent. of anhydride in a sealed tube at 100°, sulphurous anhydride is formed, together with a substance soluble in water. On removing the excess of sulphuric acid by barium carbonate, and evaporating the solution, a black residue is left which, after purification by redissolving in water, appears to have the composition $C_6H_4S_2O_3$; this the author regards as *trihydroxyphenylenic bisulphide*, $C_6H(OH)_3S_2$ [$(OH)_3 : S_2 = 1:2:4:3:5$]. It is insoluble in benzene and acetic acid, but soluble in alcohol and water, giving to the solutions a red colour. It forms insoluble substances with all acids and neutral salts, and acts as a dye to silk, wool, or cotton, with or without a mordant.

When a solution of this compound is treated with baryta, a substance is precipitated having the composition $(C_6HS_2O_3)_2Ba$, and on evaporating the aqueous solution, after treatment with carbonic anhydride, a crystalline compound $(C_6HS_2O_3)_2Ba_3$ is obtained; this when boiled with acetic anhydride, gives a *diacetyl* derivative, but if heated at 150° with this reagent, a *triacetyl* derivative is produced. These products were not, however, obtained pure.

When heated with orthotoluidine, metanitraniline, or aniline in presence of nitrous acid, compounds were obtained in which 1 molecule of the amine appeared to enter into combination with 2 molecules of the substance.

Dithionyldiphenylene, $C_6H_4{:}(SO)_2{:}C_6H_4$, melts at 237° (Friedel and Crafts, Abstr., 1889, 242, give it as 241°).

Dinitrodiphenylene bisulphide, obtained by heating a mixture of nitrobenzene, aluminium chloride, and sulphur chloride, is a crystalline substance, of a violet colour, which melts at 112° and decomposes at about 150°. It is very slightly soluble in water, but is soluble in alcohol, benzene, and acetic acid, and is of no use as a permanent dye.

Ditolylenic bisulphide, $C_6H_3Me{:}(S)_2{:}C_6H_3Me$, formed by heating toluene with aluminium chloride and sulphur chloride, is viscous at ordinary temperatures, and boils at 248—250° under 15 mm. pressure. It is insoluble in water, but soluble in alcohol, benzene, toluene, and acetic acid. Its solution in sulphuric acid is of a brilliant violet colour.

Ditolylene disulphone, $C_6H_3Me{:}(SO_2)_2{:}C_6H_3Me$, is obtained by treating a boiling solution of ditolylenic bisulphide with chromic acid. It melts at 184°, and is soluble in acetic acid. Its solution in sulphuric acid is colourless.

M. W. T.

Normal Diazo-compounds. By ARTHUR R. HANTZSCH (*Ber.*, 1897, **30**, 339—347).—Bamberger's statement (Abstr., 1896, 299; this vol., i, 217) that normal metallic diazo-salts are scarcely, or comparatively slightly, attacked by sodium amalgam, whereas the iso-salts are readily reduced to hydrazines, is incorrect. The normal salts, if

prepared in solution by Schraube's method (pouring a 20—25 per cent. solution of the diazo-chloride, &c., into 40 times its weight of 50 per cent. potassium hydroxide), are readily reduced to hydrazines by sodium amalgam at 0°; and by extracting at once with ether, and evaporating the extract, the hydrazines are obtained in the pure state. The yield is quite as good as with the iso-salt. The reduction may also be effected with zinc dust in alkaline solution, and this agent is further capable of reducing both normal and iso diazo-sulphonates and diazo-cyanides. The solution of normal diazo-salt prepared by Bamberger's method, when it is treated with sodium amalgam, does not lose its power of forming azo-dyes for several hours; during this time, the hydrazine which is at first formed becomes converted into resinous substances. It is formed, however, and it is unaccountable that Bamberger should have overlooked it. The argument for the *structural* isomerism of normal and iso (*syn-* and *anti-*) diazo-salts which he based on their different behaviour towards sodium amalgam is thus devoid of foundation.

Apparently conclusive proof is given that the normal sodium diazo-salt of diazosulphanilic acid prepared by the author was really pure. Bamberger always obtained it mixed with sodium hydroxide, and this is why his determinations of the electrical conductivity gave results which were too high. C. F. B.

Behaviour of Aromatic Diazo-chlorides towards Benzylideneamidoguanidine. By EDGAR WEDEKIND (*Ber.*, 1897, **30**, 444—449).—Thiele has shown (Abstr., 1892, 1295), that amidoguanidine resembles phenylhydrazine in its behaviour towards aldehydes and ketones, and the author now shows that this is also true of its action on diazo-salts.

Guanazylbenzene, $NPh:N\cdot CPh:N\cdot NH\cdot C(NH_2):NH$, is obtained by adding diazobenzene chloride to a cooled solution of benzylideneamidoguanidine in dilute alcohol; it crystallises in orange prisms, and melts at 199°.

According as substitution takes place in the free benzene nucleus or in that introduced by the diazo-salt, the isomerides are distinguished by the symbols I and II.

Meta-II-nitroguanazylbenzene,

$$NO_2\cdot C_6H_4\cdot N:N\cdot CPh:N\cdot NH\cdot C(NH_2):NH,$$

is prepared from metanitrodiazobenzene chloride and benzylideneamidoguanidine, and crystallises in orange needles melting at 206°. *Meta-II-amidoguanazylbenzene* is formed on reducing it with stannous chloride; it crystallises in brownish-yellow needles, and melts at 193°.

Paranitrobenzylideneamidoguanidine crystallises in dark red prisms, and melts at 206°.

Para-I-nitroguanazylbenzene,

$$NPh:N\cdot C(C_6H_4\cdot NO_2):N\cdot NH\cdot C(NH_2):NH,$$

is a brownish-yellow powder which melts at 209°; the solution in concentrated sulphuric acid is first yellow, and then darkens, gradually becoming violet. M. O. F.

Acidyl-nitrosamines. By EUGEN BAMBERGER (*Ber.*, 1897, **30**, 366—384).—Nitrosoacetanilide, and compounds of a more or less similar constitution, exhibit many analogies to diazo-compounds.

Nitrosoacetanilide reacts with benzene, for example, in the following manner—$C_6H_5\cdot NAc\cdot NO + C_6H_6 = C_6H_5\cdot C_6H_5 + N_2 + HAc$. With thiophen, it reacts in a similar manner; in one experiment, when the substances were mixed at 0°, and the mixture at once withdrawn from the refrigerator, an explosion took place almost before the mixture had attained the ordinary temperature of the room. In carrying out the reaction, the two substances are mixed at −10°, at 0°, or at the ordinary temperature, sometimes in ethereal solution, and are allowed to remain a day or two if action does not take place at once. In some cases, where the reacting substances are not mutually soluble, they are shaken together for some time.

Nitrosoacetanilide with benzene yields diphenyl; with toluene, it yields a mixture of ortho- and para-phenyltolyl; with thiophen, β-phenylthiophen, $C_6H_5\cdot C_4SH_3$, which melts at 90—90·5° after repeated recrystallisation. With sodium methoxide, it yields methylic benzenediazotate, $C_6H_5\cdot N_2\cdot OMe$; with commercial potassium sulphite ("*kalium sulphurosum*"), it gives the diazosulphonate, $C_6H_5\cdot N_2\cdot SO_3K$, but with potassium sulphite, freshly prepared by saturating aqueous potassium carbonate with sulphurous anhydride at −5° and then neutralising with solid potassium carbonate, it yields *potassium phenylhydrazinedisulphonate* (following abstract). Ethylic nitrosomethylcarbamate, $COOEt\cdot NMe\cdot NO$, yields α- and β-naphthylic methylic ethers with α- and β-naphthol respectively. Parachloro- and parabromonitrosoacetanilide and nitrosodiphenylcarbamide, $NHPh\cdot CO\cdot NPh\cdot NO$, all react with benzene, yielding parachloro- and parabromo-diphenyl and diphenyl respectively. C. F. B.

Potassium Phenylhydrazinedisulphonate. By EUGEN BAMBERGER and ALEXANDER MEYENBERG (*Ber.*, 1897, **30**, 374—378).—This substance, $C_6H_5\cdot N(SO_3K)\cdot NH\cdot SO_3K$, can be prepared by shaking with a freshly prepared solution of potassium sulphite, either nitrosoacetanilide (compare preceding abstract), potassium benzenediazosulphonate, $C_6H_5\cdot N\colon N\cdot SO_3K$, or potassium benzeneisodiazotate, $C_6H_5\cdot N\colon N\cdot OK$; the last method is the most convenient. It crystallises in white needles, and is readily soluble in water; it does not reduce Fehling's solution; when heated with very dilute hydrochloric acid, it yields the monosulphonate, $C_6H_5\cdot NH\cdot NH\cdot SO_3K$, but with strong hydrochloric acid it gives phenylhydrazine; heating with alkalis converts it first into the diazosulphonate, and finally into potassium sulphanilichydrazosulphonate, $SO_3K\cdot C_6H_4\cdot NH\cdot NHSO_3K$ (compare von Pechmann, Abstr., 1895, i, 370). C. F. B.

Isomeric Amidines. By REINHOLD WALTHER (*J. pr. Chem.*, 1897, [ii], **55**, 41—48).—*Phenylparatolylmethenylamidine*,

$$NPh\colon CH\cdot NH\cdot C_6H_4Me,$$

melting at 120°, is formed by the action of paratoluidine on diphenylmethenylamidine; the isomeric substance, $C_6H_4Me\cdot N\colon CH\cdot NHPh$, melting at 132°, is obtained when aniline hydrochloride is heated with diparatolylmethenylamidine in alcoholic solution. The yellow platinochlorides of both substances were prepared.

When formotoluidide is heated with aniline in the presence of phosphorus oxychloride, the product melts at 98°, its yellow platinochloride

at 207°. Formanilide and paratoluidine yield a product which melts at 102°, its yellow platinochloride at 218°. These two substances are obviously not identical with the two first mentioned, as one would have expected them to be; it is, perhaps, a case of stereoisomerism.

C. F. B.

Paraisobutylphenoxyacetic Acid. By WALTER P. BRADLEY and F. KNIFFEN (*Amer. Chem. J.*, 1897, **19**, 70—76).—*Paraisobutylphenoxyacetic acid*, $C_4H_9 \cdot C_6H_4 \cdot O \cdot CH_2 \cdot COOH$, is formed when the sodium salt of paraisobutylphenol is fused with sodium chloracetate. It separates from light petroleum in radiating crystals, and melts at 86·5°. The *barium* and *magnesium* salts are both crystalline; the *methylic* salt could not be obtained crystalline, but is converted by ammonia into the *amide*, which crystallises in snow-white plates melting at 134°. The *anilide* forms long needles and melts at 97°; whilst the *metanitranilide* crystallises in cream-coloured needles and melts at 136—139°. Nitric acid converts the anilide into a *tetranitranilide*, which forms nodular, yellow crystals and melts gradually between 135° and 140°; alcoholic potash hydrolyses it with formation of orthoparadinitraniline, so that two of the nitro-groups are situated in each of the benzene nuclei.

The *orthotoluidide* of the acid crystallises in long, white plates melting at 91°, and the *paratoluidide* forms similar crystals melting at 122°.

The *phenylhydrazide* is colourless, and melts at 171·5°. A. H.

Non-existence of two Orthophthalic Acids. By HENRY L. WHEELER (*Amer. Chem. J.*, 1896, **18**, 829—836).—Experiments previously made by Howe (Abstr., 1896, i, 480), by which β-phthalic acid is said to have been prepared, have been carefully repeated with pure materials, but in no case could the acid be obtained.

It is pointed out that Howe's errors are not confined to experimental work, but that the calculated figures for several of his analytical results are wrong, and, moreover, several statements by other authors are inaccurately quoted.

As β-phthalic acid itself could not be obtained, the methods he gives for obtaining its derivatives could not be repeated.

A. W. C.

Two Isomeric Chlorides of Orthosulphobenzoic Acid. By IRA REMSEN (*Amer. Chem. J.*, 1896, **18**, 791—794. Compare Abstr., 1895, i, 472).—A *résumé* of recent work on the two isomeric chlorides embodied in the two following abstracts. A. W. C.

Purification of the Chlorides of Orthosulphobenzoic Acid, and the action of various Reagents on them. By IRA REMSEN and S. R. MCKEE (*Amer. Chem. J.*, 1896, **18**, 794—809. Compare Abstr., 1895, i, 472, 473).—Improvements in methods of preparation and separation of the two chlorides are given. The symmetrical compound, $COCl \cdot C_6H_4 \cdot SO_2Cl$ melts at 79—79·5° (uncorr.), not at 76° as previously stated; whereas the unsymmetrical compound, $C_6H_4{<}^{CCl_2}_{SO_2}{>}O$, melts at 21·5—22·5°. When treated with water, both substances yield the same orthosulphobenzoic acid, the chloride of lower melting point being much more rapidly acted on than that of high melting point.

Phenol converts the chloride of high melting point into diphenylic orthosulphobenzoate, a new substance, *phenylic orthosulphaminebenzoate* melting at 131—132° (uncorr.), and an intermediate product which could not be isolated, being produced at the same time. The same substances are obtained from the mixed chlorides or the chloride of lower melting point.

Diphenylic orthosulphaminebenzoate, when treated with ammonia, gives the ammonium salt of benzoicsulphinide, and with hydrochloric acid and alcoholic potash, orthosulphobenzoic acid and its potassium salt respectively.

With resorcinol, both chlorides yield the same sulphonefluorescein, whilst with aniline, the chloride of higher melting point gives the fusible anilide, and that of low melting point a mixture of the fusible and infusible anilides. Ammonia and the chloride of high melting point yield the ammonium salt of benzoicsulphinide, whereas the one of lower melting point is partially transformed into the chloride of higher melting point, and partially into ammonium orthocyanobenzenesulphonate (see below). Both chlorides yield orthobenzoyldiphenylsulphone by the action of benzene and aluminium chloride.

A. W. C.

Relations of the Anilides of Orthosulphobenzoic Acid. By IRA REMSEN and J. R. HUNTER (*Amer. Chem. J.*, 1896, **18**, 809—818. Compare Abstr., 1895, i, 472, 473).—By the action of aniline on the mixed chlorides of orthosulphobenzoic acid, two anilides, a fusible and an infusible, are obtained; with benzoic chloride, the infusible anilide yields orthosulphobenzanil and benzanilide. From this and various other reactions which the authors have studied, they conclude that the two aniline residues remain intact in the infusible anilide, which is represented by the formula $C_6H_4{<}{\genfrac{}{}{0pt}{}{C(NHPh)_2}{SO_2}}{>}O$.

Orthosulphobenzodianil, $C_6H_4{<}{\genfrac{}{}{0pt}{}{C(:NPh)}{SO_2}}{>}NPh$, produced by the action of phosphorus oxychloride or phosphoric anhydride on either anilide, or by the action of phosphorus pentachloride on the infusible anilide, crystallises in brilliant, monoclinic prisms melting at 189·5° (uncorr.). Sodium hydroxide, dilute or concentrated, is without action on it, but when boiled with alcoholic potash or glacial acetic acid, it is converted into the infusible anilide, whilst concentrated hydrochloric acid converts it into orthosulphobenzanil. A. W. C.

Orthocyanobenzenesulphonic Acid. By IRA REMSEN and W. J. KARSLAKE (*Amer. Chem. J.*, 1896, **18**, 819—828. Compare preceding abstracts).—*Ammonium orthocyanobenzenesulphonate* is obtained by the action of ammonia on the mixed chlorides of orthosulphobenzoic acid, and on heating this ammonium salt with sodium, potassium, or barium hydroxide, the corresponding well-crystallised sodium, potassium, or barium salt is obtained. All attempts to isolate the free acid proved unsuccessful; barium orthocyanobenzenesulphonate when treated with dilute sulphuric acid yielding orthobenzaminesulphonic acid. *Ammonium orthobenzaminesulphonate* is produced by treating ammonium orthocyanobenzenesulphonate with dilute hydrochloric acid; it crystallises in thin, transparent needles melting at 219—220°

(uncorr.). *Potassium*, *sodium*, *barium*, *calcium*, and basic *lead* salts, prepared by the action of the corresponding hydroxides on ammonium orthocyanobenzenesulphonate, are also described.

Acid ammonium orthosulphobenzoate may be obtained from ammonium orthocyanobenzenesulphonate by heating the latter in sealed tubes with hydrochloric acid. A. W. C.

Benzoylcarbinol. By ARNOLD VOSWINKEL (*Chem. Centr.*, 1896, i, 764—765; from *Pharm. Centr.*, H., **37**, 103—105).—In connection with the work of V. Fritz (Abstr., 1896, i, 151), the author describes his own researches. *Benzoylmethylic salicylate*, $OH\cdot C_6H_4\cdot COO\cdot CH_2Bz$, or *salhypnone*, is prepared by the action of sodium salicylate on α-bromacetophenone. It crystallises in long, colourless needles, melts at 113—114°, and is insoluble in water; it reduces Fehling's solution, and on heating with dilute alkalis yields benzaldehyde. It has no special physiological action. The *oxime*, obtained by the action of hydroxylamine hydrochloride in presence of potassium hydroxide, crystallises in needles melting at 97°, whilst the *hydrazone* melts at 133°. On heating to 230—240°, benzoylmethylic salicylate decomposes into phenol, carbonic anhydride, and acetophenone. By the action of dilute hydrochloric acid, crystals are obtained which reduce Fehling's solution and with ferric chloride give a violet coloration; the formula of this new compound is probably $OH\cdot C_6H_4\cdot COO\cdot CH_2\cdot CPh(OEt)_2$.

E. W. W.

Schiff's Reaction for Aldehydes. By G. URBAIN (*Bull. Soc. Chim.*, 1896, [iii], **15**, 455—456).—It is generally supposed that the restoration of the colour of Schiff's reagent (magenta decolorised by sulphurous acid) by aldehydes is due to the regeneration of the magenta. The author shows that it is really due to the formation of coloured compounds, by the condensation of the aldehyde and the magenta.

M. W. T.

Diphthalylethylene; an Analogue of Indigo in the Indene Series. By VICTOR KAUFMANN (*Ber.*, 1897, **30**, 382—387).—When diketohydrindene is oxidised with dilute hydrogen peroxide or potassium persulphate in alkaline solution, several oxidation products are produced which are analogous to indigo in constitution.

Diphthalylethane, $C_6H_4<{CO \atop CO}>CH\cdot CH<{CO \atop CO}>C_6H_4$, crystallises from boiling aniline in microscopic, yellow needles, is sparingly soluble in most solvents, and melts and decomposes above 200°. The *potassium* derivative, $C_{18}H_9KO_4$, which is produced in the reaction, is a dark-green, crystalline powder.

Diphthalylethylene (*indenigo*), $C_6H_4<{CO \atop CO}>C:C<{CO \atop CO}>C_6H_4$, forms sparingly soluble red needles, which sublime above 200°, and at the same time partially decompose. It dissolves without decomposition in concentrated sulphuric acid, but is insoluble in aqueous alkalis.

Triketohydrindene (*indanetrione*), which probably has the formula $C_6H_4<{CO \atop CO}>CO$, was obtained in very small quantity. It crystallises

in brownish-yellow plates, and melts and decomposes at 190—206°. A fourth product, also obtained in extremely small quantity, was probably *orthoxalylbenzoic acid* (*2-phenethylonoic-1-methyloic acid*),

$$COOH \cdot C_6H_4 \cdot CO \cdot COOH.$$

Attempts to prepare similar compounds from the sodium compound or the bromine derivatives of diketohydrinene proved unsuccessful.

A. H.

Terpenes. By ALBERT REYCHLER (*Bull. Soc. Chim.*, 1896, [iii], 15, 366—376. Compare Abstr., 1896, i, 308).—Details are supplied which relate to the behaviour of terpenes towards trichloracetic acid (*loc. cit.*); the preparation of camphene from pinene hydrochloride and the conversion of that hydrocarbon into isoborneol are also described.

Camphene hydrochloride and isobornylic chloride melt at 149—151° and 150—152° respectively, whilst bornylic chloride melts at 157—159°; the author ascribes to these substances the same structural formula, regarding the two former as identical, whilst bornylic chloride is stereoisomeric with them.

M. O. F.

The Thujone Series. By OTTO WALLACH (*Ber.*, 1897, 30, 423—428. Compare Abstr., 1893, i, 105, 107).—Oxidation of thujone (tanacetone) gives rise to α- and β-thujaketonic (tanacetoketonic) acids (*loc. cit.*); the oxime of the α-modification (m. p. 168°) gives rise to the *compound* $C_{10}H_{16}O_2$:NOH,HCl, and the *compound* $C_{10}H_{16}O_2$:NOH,HBr, which melt at 128—129° and 176—177° respectively. Whilst alkali hypobromite converts α-thujaketonic acid into Semmler's tanacetogendicarboxylic acid (m. p. 141·5°), the β-acid gives rise to an unsaturated, isomeric *acid*, $C_9H_{14}O_4$, which melts at 113—114°; this observation confirms the author's former conclusion in regarding the β-acid as unsaturated, but the α-acid is saturated, and is so constructed as to yield an ethylene linking under the influence of acids and high temperature.

Methylheptylene ketone, $C_9H_{16}O$ (Abstr., 1893, i, 107, 597), obtained by distilling the thujaketonic acids, forms the *semicarbazone* which melts at 143°, and the *benzylidene* derivative, which crystallises in white needles, and melts at 170°; reduction converts the ketone into an alcohol, C_9H_{17}·OH, which is oxidised by permanganate to the *glycerol*, $C_9H_{17}(OH)_3$, a syrupy liquid which boils at 160—165° under a pressure of 10 mm. Hot, dilute sulphuric acid converts the glycerol into the *oxide*, $C_9H_{16}O$, which has the odour of pinole, and boils at 160—165°; the *bromo*-derivative, $C_9H_{15}BrO_2$, crystallises from alcohol in white needles, and melts at 124·5°.

Isothujaketonic acid, $C_{10}H_{16}O_3$, is obtained by oxidising isothujone (Abstr., 1895, i, 620) with potassium permanganate; it is a saturated compound, and boils at 142—143° under a pressure of 12 mm., and at 271—273° under atmospheric pressure; the *semicarbazone* melts at 193°, and the *oxime* at 153°. Sodium hypobromite converts isothujaketonic acid into isopropylsuccinic acid with elimination of bromoform.

Thujamenthone, $C_{10}H_{18}O$, more closely resembles menthone than tetrahydrocarvone, being isomeric with both substances. When oxidised with potassium permanganate, it yields the ketonic *acid*, $C_{10}H_{18}O_3$, which forms a *semicarbazone* melting at 174·5°; sodium hypobromite converts the ketonic acid into the dibasic *acid*, $C_9H_{16}O_4$, which

melts at 134·5°. On oxidation with chromic acid, thujamenthone gives rise to the ketonic *lactone*, $C_{10}H_{16}O_3$, which melts at 41°; the *oxime* melts at 156°.

Accepting for thujone the formula $\begin{array}{l} CHPr^{\beta}\cdot CH\cdot CO \\ | \quad\quad\quad\; | \quad\;\; | \\ CH_2 - CH\cdot CHMe \end{array}$ (Semmler, Abstr., 1894, i, 339), the author represents isothujone and isothujaketonic acids by the formulæ

$CHPr^{\beta}<\begin{array}{l}CH:CH\\CH_2\cdot CO\end{array}>CHMe$ and $COOH\cdot CH_2\cdot CHPr^{\beta}\cdot CH:CH\cdot COMe$ respectively. M. O. F.

Tanacetoketonic (Thujaketonic) Acid. By J. C. W. Ferdinand Tiemann and Friedrich W. Semmler (*Ber.*, 1897, **30**, 429—443. Compare foregoing abstract).—α-Tanacetoketonic (thujaketonic) acid, $\begin{array}{l} CHPr^{\beta}\cdot CH\cdot COOH \\ | \quad\quad\quad\; | \\ CH_2 - CH\cdot COMe \end{array}$, arises from tanacetone (thujone) under the influence of a 2 per cent. solution of potassium permanganate, and melts at 74·5°; the oxime melts at 168°, and alkali hypobromite converts the acid into tanacetogendicarboxylic acid, $\begin{array}{l} CHPr^{\beta}\cdot CH\cdot COOH \\ | \quad\quad\quad\; | \\ CH_2 - CH\cdot COOH \end{array}$, which melts at 141—142°.

β-Tanacetoketonic (*3-methoethyl-2-heptene-6-onoic*) *acid*,

$$COOH\cdot CH:CPr^{\beta}\cdot CH_2\cdot CH_2\cdot COMe,$$

is produced on heating an aqueous solution of the α-acid during a protracted period, and is rapidly formed when the acid is heated at 150° under reduced pressure; it melts at 78°, and the oxime melts at 103—104°.

β-Tanacetogendicarboxylic (*3-Methoethyl-2-hexenedioic*) *acid*,

$$COOH\cdot CH:CPr^{\beta}\cdot CH_2\cdot CH_2\cdot COOH,$$

obtained by the action of alkali hypobromite on β-tanacetoketonic acid, crystallises from water, and melts at 116—118° (compare Abstr., 1893, i, 108). *ω-Dimethyllevulinic methyl* (*isobutyrylethyl methyl*) *ketone*, or *2-methylheptan-3 : 6-dione*, $COPr^{\beta}\cdot CH_2\cdot CH_2\cdot COMe$, is produced on oxidising β-tanacetoketonic acid in alkaline solution with a 2 per cent. solution of potassium permanganate; it boils at 102—106° under a pressure of 23 mm., has the sp. gr. = 0·9402 at 20°, and the refractive index, $n_D = 1{\cdot}4321$, whence the molecular refraction M = 39·47. The *oxime* crystallises from water in prisms, and melts at 132°.

ω-Dimethyllevulinic (*2-methylhexan-3-onoic*) *acid*,

$$COPr^{\beta}\cdot CH_2\cdot CH_2\cdot COOH,$$

arises from the ketone on treating it with alkaline hypobromite, bromoform being eliminated; it melts at 32°, and boils at 145—146° under a pressure of 20 mm. The acid is also produced when β-tanacetogendicarboxylic acid is oxidised with potassium permanganate.

2-Methyl-5-isopropylpyrroline, $NH<\begin{array}{l}CMe:CH\\CPr^{\beta}:CH\end{array}$, is obtained by heating the diketone with alcoholic ammonia in sealed tubes at 180° for 2 hours; it has the sp. gr. = 0·9051 at 20°, and the refractive index n_D = 1·4988, whence the molecular refraction M = 39·86.

Tanacetoketone (thujaketone, or *2-methyl-3-metheneheptane-6-one*),

$CH_2{:}CPr^{\beta}{\cdot}CH_2{\cdot}CH_2{\cdot}COMe$, arises from β-tanacetoketonic acid by elimination of carbonic anhydride, and when oxidised with potassium permanganate yields a small proportion of ω-dimethyllevulinic methyl ketone; the chief product, however, is the ketone glycol, *2-methyl-3-methylolheptan-6-one-3-ol*, $OH{\cdot}CH_2{\cdot}CPr^{\beta}(OH){\cdot}CH_2{\cdot}CH_2{\cdot}COMe$.

Tanacetogen dioxide, $CPr^{\beta}\left\langle\begin{array}{c}CH_2\text{—}O\\ \text{———}O\text{———}\\ CH_2{\cdot}CH_2\end{array}\right\rangle CMe$, is produced on distilling the ketone glycol under reduced pressure, water being suddenly eliminated; it boils at 72—75° under a pressure of 19 mm., has the sp. gr. $=0{\cdot}9775$ at 20°, and the refractive index $n_D = 1{\cdot}4450$, whence the molecular refraction $M = 42{\cdot}50$. The dioxide has the odour of menthole.

Interesting theoretical considerations are developed in the paper, but they do not lend themselves to condensation. M. O. F.

Geranyl Chloride. By ALBERT REYCHLER (*Bull. Soc. Chim.*, 1896, [iii], **15**, 364—366).—The author confirms Barbier's views with regard to the composition of this substance (Abstr., 1893, i, 664), and also the impossibility of removing one molecule of hydrochloric acid from it so as to obtain the compound $C_{10}H_{17}Cl$.

When the compound $C_{10}H_{18}Cl_2$, obtained by saturating geraniol with hydrogen chloride is boiled with excess of water, a product is obtained which is intermediate in composition between $C_{10}H_{18}Cl_2$ and $C_{10}H_{18}O$.

Another attempt to prepare the monochloro-derivative by passing the calculated quantity of hydrogen chloride into geraniol was equally unsuccessful. M. W. T.

Menthol and the Reduction of Menthone. By ERNST O. BECKMANN (*J. pr. Chem.*, 1897, [ii], **55**, 14—31).—The *sodium* derivative of natural *l*-menthol was prepared by heating the latter with sodium in an atmosphere of hydrogen. The benzoate and *stearate* were obtained by heating it with the acid anhydrides for several hours at 160—170°; the stearate melts at 39°.

Menthol and menthone can be separated by warming the mixture, in alcoholic solution, with hydroxylamine (? hydrochloride) and sodium hydrogen carbonate, extracting with ether, evaporating down the extract, and again extracting with dilute sulphuric acid. This leaves the menthol behind, but removes menthone oxime, from which the menthone can be regenerated by adding excess of sodium hydroxide together with ice (to avoid rise of temperature), saturating with carbonic anhydride, and extracting with ether. This method of separation does not cause any transformation into optical isomerides.

When menthone is reduced with sodium in alcoholic solution, menthol alone is formed, excess of nascent hydrogen being present. If a solvent is used which gives off no hydrogen when treated with sodium, such as ether, some *menthonepinacone*, $C_{20}H_{38}O_2$, is also formed; this melts at 94°, and in 5 per cent. alcoholic solution at 20°, in a 100 mm. tube has a rotation $\alpha_D = -0{\cdot}48°$. Whether dextro- or lævo-menthone is reduced, and whichever method of reduction is used, the product is always a mixture of menthols, and is pronouncedly lævorotatory. From this mixture, by forming the benzoates, natural *l*-menthol can be isolated, and, in

addition, an *isomenthol* which melts at 78—81°, and has a feeble specific rotation, $[\alpha]_D = +2°$, in 20 per cent. alcoholic solution. The compound of natural menthol with phenylcarbimide, when hydrolysed with alcoholic sodium ethoxide at 150°, yields some *inactive menthol* melting at 49—51°.

In the reduction of menthol with sodium in ethereal solution, only 1 atom of sodium could be used for each molecule of menthol, this being all that would dissolve; on treating the product with water, a mixture of menthol and menthone in molecular proportion is obtained. The ethereal solution is then dried, and again treated with sodium (1 atom) when a complete reduction to menthol occurs, in accordance with the equation

$$C_{10}H_{19}\cdot OH + C_{10}H_{18}O + 2Na = 2C_{10}H_{19}\cdot ONa.$$

To ensure complete reduction, however, a third treatment with sodium is resorted to.

Stearic anhydride can be prepared conveniently by suspending the dry sodium salt of commercial stearic acid in benzene, adding the calculated quantity of phosphorus oxychloride, filtering from the sodium chloride formed, and evaporating the benzene. C. F. B.

Borneol and the Reduction of Camphor. By ERNST O. BECKMANN (*J. pr. Chem.*, 1897, [ii.], **55**, 31—40).—When camphor is reduced with sodium in boiling alcoholic solution (ethylic or amylic alcohol, or phenol) much more borneol than isoborneol is formed; the boiling point of the solution has little influence. In solution in ether, light petroleum, and cold or boiling toluene, almost as much isoborneol as borneol is formed; the amounts of these present is calculated from the specific rotation of the mixture, that of the pure components being known.

C. F. B.

Camphor, III. and IV. By J. C. W. FERDINAND TIEMANN (*Ber.*, 1897, **30**, 321—331, 404—422. Compare this vol., i, 161, 199).—*Isoamidocamphor*, $CH\begin{cases} CH_2\text{———}CO \\ \text{———}\ CH_2\ \text{———} \\ CMe_2\cdot CHMe_2 \end{cases}C\cdot NH_2$, is obtained by adding concentrated sulphuric acid to camphoroxime suspended in water, extracting the diluted liquid with ether in order to remove campholenonitrile, and finally rendering alkaline with caustic soda; it is more conveniently prepared by treating camphoroxime with twice its weight of hydriodic acid (sp. gr. = 1·96). It crystallises in prisms, and melts at 39° to an oil which boils at 120°, 133—135°, and 254°, under pressures of 10 mm., 25 mm., and 760 mm., respectively; the base is optically inactive, and is indifferent towards ammoniacal silver and Fehling's solutions. The *benzylidene* and *benzoyl* derivatives melt at 98° and 128° respectively, the *hydrochloride* at 89°, and the *oxalate* at 145°; the *platinochloride* forms bright yellow crystals, and the *aurochloride* dissolves in ether, and crystallises in reddish-yellow leaflets. *Dimethylisoamidocamphor* crystallises in needles and boils at 268—274°; the *hydrochloride* melts at 140°, the *platinochloride* crystallises in yellow needles, and the *hydriodide* forms colourless, lustrous leaflets. When an aqueous solution of isoamidocamphor hydrochloride is heated almost at the boiling point, β-campholenamide is produced, but if the applica-

tion of heat is maintained for some time, dihydrocampholenolactone is formed. The saturated character of the base, and the resemblance which its chemical and physical properties bear to those of amidocamphor, seem to indicate the existence of a double ring in the former compound, and the author represents its production from camphoroxime by the following steps.

$$1.\ \mathrm{CH}\left\langle\begin{array}{c}\mathrm{CH_2\cdot C(NOH)}\\ \text{——}\mathrm{CH_2}\text{——}\\ \mathrm{CMe_2\cdot CHMe}\end{array}\right\rangle\mathrm{CH}. \qquad 2.\ \mathrm{NOH{:}CH\cdot CH_2\cdot CH}\Big\langle\begin{array}{l}\mathrm{CH_2—CH}\\ \mathrm{CMe_2\cdot CMe}\end{array}$$

$$3.\ \mathrm{CN\cdot CH_2\cdot CH}\Big\langle\begin{array}{l}\mathrm{CH_2—CH}\\ \mathrm{CMe_2\cdot CMe}\end{array}. \qquad 4.\ \mathrm{NH_2\cdot CO\cdot CH_2\cdot CH}\Big\langle\begin{array}{l}\mathrm{CH{=}CH}\\ \mathrm{CMe_2\cdot CHMe}\end{array}.$$

$$5.\ \mathrm{CH}\left\langle\begin{array}{c}\mathrm{CH_2\text{———}CO}\\ \text{——}\mathrm{CH_2}\text{——}\\ \mathrm{CMe_2\cdot CHMe}\end{array}\right\rangle\mathrm{C\cdot NH_2}.$$

Dihydrocampholenimide, $\mathrm{CH}\left\langle\begin{array}{c}\mathrm{CH_2\cdot CO\cdot NH}\\ \text{——}\mathrm{CH_2}\text{——}\\ \mathrm{CMe_2\cdot CHMe}\end{array}\right\rangle\mathrm{CH}$, is obtained by distilling isoamidocamphor under atmospheric pressure in such a manner that the substance is slightly superheated; it crystallises in white needles, melts at 108°, and boils at 266°. The prolonged action of cold mineral acids eliminates ammonia, and gives rise to dihydrocampholenolactone, whilst boiling, concentrated alkalis convert the substance into β-campholenamide.

Hydroxydihydrocampholenamide, $\mathrm{NH_2\cdot CO\cdot CH_2\cdot CH}\Big\langle\begin{array}{l}\mathrm{CH_2—CH\cdot OH}\\ \mathrm{CMe_2\cdot CHMe}\end{array}$, is the intermediate product in the conversion of dihydrocampholenimide into β-campholenamide, and is obtained by keeping isoamidocamphor in the moist condition during several months; it sublimes without undergoing decomposition, and melts at 184°.

The *compound*, $C_{10}H_{17}NO_2$, is obtained by the action of hydroxylamine on isoamidocamphor hydrochloride in aqueous solution; it crystallises from alcohol in white prisms, and melts at 165°. When isoamidocamphor is treated with boiling water, ammonia is eliminated, and dihydrocampholenolactone produced; the latter substance is also formed when dimethylisoamidocamphor is treated with boiling water, dimethylamine being set free. Isoamidocamphor hydrochloride, on distillation, yields ammonium chloride and an oil which boils at 230—243°.

Dihydrocampholenolactone, $\mathrm{CH}\left\langle\begin{array}{c}\mathrm{CHMe\cdot CMe_2}\\ \text{——}\mathrm{CH_2}\text{——}\\ \mathrm{O\cdot CO—CH_2}\end{array}\right\rangle\mathrm{CH}$, arises from camphoroxime in varying quantity whenever the substance is treated with concentrated acids. It is obtained in almost quantitative amount when the oxime is decomposed with moderately concentrated sulphuric acid, the liquid diluted with water, and then boiled for some time. In this change, α-campholenonitrile is first produced, and passes immediately into the β-modification, which is hydrolysed to β-campholenamide. Condensation converts the amide into isoamidocamphor, from which, in acid solution, ammonia is eliminated, giving rise to dihydrocampholenolactone. Both campholenic acids are rapidly converted

into the lactone, when treated with boiling, concentrated hydrochloric acid. The action of alcoholic and aqueous alkalis, however, is less decisive, and hydroxydihydrocampholenic acid forms an intermediate product.

It invariably happens that dihydrocampholenolactone, when prepared from camphoroxime, is contaminated with the campholenic acids, which are best removed by passing ammonia into an ethereal solution of the lactone; the filtered liquid is then agitated with dilute sulphuric acid, and the lactone, after removing the ether, distilled under reduced pressure. Dihydrocampholenolactone melts at 30° to a colourless oil, which boils at 139°, under a pressure of 18 mm., and at 256° under atmospheric pressure; it has the sp. gr. = 1·0303, and refractive index, $n_D = 1{\cdot}46801$, whence the molecular refraction $M = 45{\cdot}79$. The lactone is optically inactive, and the activity displayed by Béhal's preparation must be attributed to the presence of α-campholenic acid.

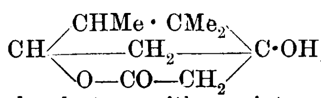
Syn-Hydroxydihydrocampholenic acid,

$$COOH\cdot CH_2\cdot CH<\begin{matrix}CH_2-CH\cdot OH\\ CMe_2\cdot CHMe\end{matrix},$$

obtained by hydrolysing the foregoing lactone with boiling caustic soda, crystallises from ether on the addition of petroleum in slender, white needles, melting at 105°; when heated above the melting point, water is eliminated from the acid, and even at ordinary temperatures, the substance gradually passes into the lactone. The *ammonium* salt melts at 138°, the *sodium* salt does not melt below 250°, and the *basic sodium* salt crystallises from a mixture of alcohol and ether, and melts at 89°.

Anti-Hydroxydihydrocampholenic acid is produced when pinonic acid is heated with concentrated alcoholic potash for several hours at 280°; it crystallises in white needles having the appearance of the *syn*-modification, and melts at approximately the same temperature as that substance, but water is not eliminated under the influence of heat, and the acid may be distilled without undergoing decomposition.

Syn-Hydroxydihydrocampholenic acid is slowly attacked by a boiling solution of potassium permanganate, yielding acetic, oxalic, and isobutyric acids, along with methyl isopropyl ketone; the same products are obtained on oxidising dihydrocampholenolactone in alkaline solution.

β-Hydroxydihydrocampholenolactone, 

is obtained by oxidising dihydrocampholenolactone with a mixture of chromic and sulphuric acids; it crystallises from water, melts at 144°, and boils at 273—275°.

βδ-Dihydroxydihydrocampholenic acid,

$$COOH\cdot CH_2\cdot C(OH)<\begin{matrix}CH_2-CH\cdot OH\\ CMe_2\cdot CHMe\end{matrix},$$

is a highly unstable compound produced on hydrolysing the foregoing lactone, and passes so readily into that substance that no definite melting point can be recorded; according to the quantity of lactone present in the specimen, it melts indefinitely at 91—127°.

It has been previously stated that the oxidation of dihydrocampholenolactone with chromic acid leads ultimately to isoketocamphoric, isocamphoronic, and terebic acids; this statement must, however, be withdrawn, the mixture of acids in question arising from a specimen of the lactone contaminated with α-campholenic acid.

Nitrodihydrocampholenolactone, $CH\begin{array}{c} \diagup CHMe\cdot CMe_2 \diagdown \\ \text{———} CH \text{———} \\ \diagdown O-CO-CH_2 \diagup \end{array}C\cdot NO_2$, is obtained by the action of dilute nitric acid on dihydrocampholenolactone, and melts at 175°; it was first obtained by Kachler and Spitzer, who described it as nitrocampholenic acid, its lactonic character being recognised by Béhal and Blaise (Abstr., 1896, i, 55).

Amidodihydrocampholenolactone, $CH\begin{array}{c} \diagup CHMe\cdot CMe_2 \diagdown \\ \text{———} CH_2 \text{———} \\ \diagdown O-CO-CH_2 \diagup \end{array}C\cdot NH_2$, arises from the nitro-lactone under the influence of reducing agents; the *hydrochloride* melts at 250°. When this base is treated with nitrous acid, campholenolactone is produced, and not, as might be anticipated, β-hydroxydihydrocampholenolactone; this change is analogous to the conversion of amidocamphor into camphenone.

γ-Bromodihydrocampholenolactone, $CH\begin{array}{c} \diagup CHMe\cdot CMe_2 \diagdown \\ \text{———} CHBr \text{———} \\ \diagdown O-CO-CH_2 \diagup \end{array}CH$, obtained by the action of bromine on β-campholenic acid, crystallises from alcohol in prisms melting at 146°.

Campholenoxidic acid, $\begin{array}{l} COOH\cdot CH_2\cdot CH\text{—————}CH \\ \qquad\qquad\;\; CMe_2\cdot CHMe\cdot CH \end{array}\!\!>O$, is produced on hydrolysing the bromo-lactone, and crystallises from a mixture of chloroform and petroleum in needles melting at 128—129°; the *sodium* salt is sparingly soluble in caustic soda. Oxidation converts this acid into 3-dimethylhexen-2-onoic acid.

Campholenolactone, $CH\begin{array}{c} \diagup CHMe\cdot CMe_2 \diagdown \\ \text{———} CH \text{===} \\ \diagdown O-CO-CH_2 \diagup \end{array}C$, is obtained on distilling the foregoing acid, or submitting it to the action of hot acids; it melts at 32—34°, and boils at 160—161° under a pressure of 28 mm. The substance is also produced on heating nitrodihydrocampholenolactone with a solution of sodium hydrogen carbonate.

The constitutional formulæ already employed to represent dihydrocampholeno-derivatives are discussed at the termination of the paper.

M. O. F.

Campholene. By J. C. W. FERDINAND TIEMANN (*Ber.*, 1897, **30**, 594—600).—Campholene was first obtained by Delalande on heating campholenic acid with phosphoric anhydride, and subsequently by Kachler, who distilled a mixture of potassium campholate and soda-lime; Béhal produced the hydrocarbon by boiling β-campholenic acid with caustic soda (Abstr., 1895, i, 240), this being substantially the method adopted by the author (*loc. cit.*, i, 677).

Campholene, C_9H_{16}, is most conveniently prepared by boiling α- and β-campholenic acids in an apparatus which admits of slight superheating of the material, and by removing the hydrocarbon as it is produced, obviates any lowering of the boiling point of the mixture; it boils at 133—135°, has a sp. gr. = 0·8034 at 20°, and the refractive index $n_D = 1·44406$ at 20°, whence the molecular refraction $M = 41·00$.

β-Dimethyllevulinic acid, $CH_3·CO·CMe_2·CH_2·COOH$, is obtained on oxidising campholene with a 2 per cent. solution of potassium permanganate at 60°; oxidation with akaline hypobromite eliminates bromoform, and gives rise to unsymmetrical dimethylsuccinic acid. The *semicarbazone* crystallises from hot alcohol, and melts at 190°.

Although, as stated by Guerbet (Abstr., 1894, i, 254), campholene yields hexahydro-ψ-cumene under the influence of concentrated hydriodic acid at 280°, the hydrocarbon cannot be regarded as a derivative of tetrahydro-ψ-cumene; its behaviour on oxidation, and the readiness with which it is obtained from the campholenic acids, point to the formula $CMe_2<\begin{matrix}CHMe·CH\\ \Vert \\ CHMe·CH\end{matrix}$ as representing its constitution.

The author does not consider that there is sufficient evidence to justify Béhal's view regarding the existence of two isomeric campholenes (Abstr., 1895, i, 240). M. O. F.

Products of Oxidation of Camphoric Acid. By LUIGI BALBIANO (*Ber.*, 1897, **30**, 289—294. Compare Abstr., 1895, i, 552 and 678).—The acid, $C_8H_{12}O_5$, obtained on oxidising camphoric acid with potassium permanganate, is regarded by the author as having the constitution $COOH·CMe<\begin{matrix}CMe_2\\ —O—\end{matrix}>CH·COOH$; this is opposed to the view of Mahla and Tiemann, who represent it by the formula

$$COOH·CHMe·CMe_2·CO·COOH$$

(Abstr., 1895, i, 679), basing their conclusion on the production of trimethylsuccinic anhydride at 170—220°, and also on the behaviour of the acid towards hydroxylamine and parabromophenylhydrazine. The author has repeated those experiments of Mahla and Tiemann which deal with the latter agent, and finds that the product is not the bromophenylhydrazone, as stated by these investigators, but an additive compound which subsequently loses $1H_2O$, and yields an anhydride devoid of the properties of a hydrazone-acid. Neither hydrochloric nor pyruvic acid eliminates bromophenylhydrazone from this substance, and on heating it at 150—160°, and distilling the product at 220—225° under a pressure of 17 mm., *3-cyano-2-methyl-3-dimethylpropanoic parabromanilide*, $CN·CMe_2·CHMe·CO·NH·C_6H_4Br$, is produced; when this is heated with hydrochloric acid for 6—8 hours at 110—120°, trimethylsuccinic acid, ammonium chloride, and parabromaniline hydrochloride are formed. *Trimethylsuccinic monoparabromanilide*,

$$COOH·CMe_2·CHMe·CO·NH·C_6H_4Br,$$

is obtained by heating the foregoing anilide with the theoretical amount of caustic soda; it crystallises from a mixture of ethylic acetate and petroleum in small, prismatic needles, and melts at 125—126°.

Further evidence against a ketonic formula for the acid $C_8H_{12}O_5$ is afforded by the indifference of the ethylic salt towards aluminium

amalgam, parabromophenylhydrazine, and hydroxylamine; the author consequently advocates the oxide formula. M. O. F.

Occurrence of Pine-resin Acids. By EBERHARD RIMBACH *Chem. Centr.*, 1896, i, 756; from *Ber. pharm. Ges.*, 6, 61—64).—The author, on examining the crystals formed on adding water to an alcoholic solution of American colophony, finds that they are not lævorotatory like abietic acid, but strongly dextrorotatory. By recrystallisation from various solvents, conversion of the acid into the insoluble sodium salt, and recrystallisation of this salt, a product is obtained which, on being decomposed by hydrochloric acid, yields crystals of a constant specific rotatory power, $[\alpha]_D = +73\cdot36°$ in chloroform solution, and melting at 210—211°; there is no doubt that this acid is identical with Vesterberg's dextropimaric acid. The molecular weight agrees with the formula $C_{20}H_{20}O_2$. From these facts, it is evident that American colophony may contain, not only abietic acid, but also considerable quantities of dextropimaric acid. In the above case, the latter was accompanied by small quantities of the former. The usual assumption that abietic and dextropimaric acids are characteristic of certain individual resins, must therefore be discarded, and an interchangeable occurrence regarded as more probable.

E. W. W.

Guaiacum Resin. By JOSEF HERZIG and F. SCHIFF (*Ber.*, 1897, 30, 378—380).—The acid of guaiacum resin yields a *diacetate*, $C_{18}H_{18}(OMe)_2(OAc)_2$, and contains two methoxy-groups, whereas Doebner and Lücker have found (this vol., i, 165) that the benzoyl-derivative is a monobenzoate. The authors propose to examine the products of distillation of the resin acid, in order to ascertain the constitution of pyroguaiacin. A. H.

Glucosides of Black and White Mustards. By J. GADAMER (*J. Pharm.*, 1896, [vi.], 4, 462—468; from *Apoth. Zeit.*, 1896, 11, 752).—Potassium myronate (sinigrin) crystallises with $1H_2O$, which it loses at 100° in a vacuum, it then having the composition $C_{10}H_{16}NS_2O_9K$; it undergoes slight decomposition during the drying, and melts at 126—127°. Its solutions are lævogyrate $[\alpha]_D = -15° 13'$. In the decomposition of the glucoside by means of myrosin, water plays a part; a portion of the ferment becomes coagulated by the potassium hydrogen sulphate formed, and is thus rendered useless, but if the acid sulphate is kept neutralised by potash, the decomposition is more complete, although the yield is always some 2 per cent. below the theoretical. The addition of feeble bases, for example, alumina, copper carbonate, or barium carbonate, facilitates the decomposition; an excess of soda or magnesium hydrogen carbonate, however, retards the fermentation.

Some of the secondary products formed are allylic sulphide and cyanide and carbon bisulphide.

Silver nitrate causes a fine crystalline precipitate of the *compound*, $C_3H_5NCS,Ag_2SO_4 + H_2O$, which is the silver salt of an unstable

dibasic acid; on adding hydrochloric acid, decomposition ensues, and allylic sulphide and cyanide, together with sulphurous anhydride, are formed. Sulphuric acid acts on allylic cyanide, yielding ammonium sulphate and crotonic acid. On the addition of ammonia to the above-mentioned silver salt, it first dissolves and then a crystalline *compound*, $C_3H_5NCS,Ag_2SO_4,2NH_3$, is deposited. Barium chloride has no action on sinigrin, whereas barium hydroxide brings about complete decomposition. On account of these decompositions, the author regards sinigrin as the potassium salt of an ethereal sulphate derived from the hypothetical imidoxythiocarbonic acid in which the three hydrogen atoms are replaced by SO_2OK, $C_6H_{11}O_5$, and C_3H_5, namely, $C_3H_5\cdot N\colon C(S\cdot C_6H_{11}O_5)O\cdot SO_3K$.

Air-dried sinalbin, the glucoside of white mustard, has the composition $C_{30}H_{42}N_2S_2O_{15} + 5H_2O$; it readily loses $4H_2O$ when kept over sulphuric acid, but only gives up the last molecule when kept over sulphuric acid for 6 weeks. The air-dried compound melts at 83—84°, and the anhydrous compound at 138·5—140°. It is lævogyrate, the rotatory power of the anhydrous compound being $[\alpha]_D = -8° 30'$. Under the influence of myrosin, it combines with water, and then yields an essential oil, $C_7H_7O\cdot NCS$, sinapin hydrogen sulphate, $C_{16}H_{24}NO_5\cdot HSO_4$, and *d*-glucose. On distillation with steam, it yields thiocyanic acid and sulphur. An acid solution of mercuric sulphate yields a compound of definite composition,

$$Hg[S\cdot C(\colon N\cdot C_7H_7O)\cdot O\cdot SO_2\cdot O\cdot C_{16}H_{24}NO_5]_2,$$

which crystallises in yellowish needles and melts at 155—157°. The author controverts König's statement that white mustard contains sinigrin.

Sinapin, according to Babo and Hirschbrunn, exists in white mustard in two modifications, one of which turns red with ferric salts, whilst the other does not. The author thinks, however, that the latter modification is identical with sinalbin, whereas the former is produced by the decomposition of sinalbin in the course of its preparation by Babo and Hirschbrunn's method. Sinapin exists in black mustard in the form of its *hydrogen sulphate*, which crystallises from water on the addition of sulphuric acid. Its composition is $C_{16}H_{24}NO_5\cdot HSO_4 + 2H_2O$, and it melts at 186—188°. The *thiocyanate*, $C_{16}H_{24}NO_3\cdot SCN + H_2O$, melts at 178°. It has not been found possible to isolate the base, as it readily dissolves in water and undergoes decomposition. The normal *sulphate* crystallises with $5H_2O$, and undergoes partial decomposition at 100°. The *bromide*, $C_{16}H_{24}NO_5Br + 3H_2O$, and *iodide*, $C_{16}H_{24}NO_5I + 3H_2O$, are both sparingly soluble in water. When treated with barium hydroxide, sinapin is hydrolysed to choline and sinapic acid, $C_{11}H_{12}O_5$; the latter crystallises in yellowish needles and melts at 191—192°. When fused with potash, it yields, according to Remsen and Evale, pyrogallol, but according to the author, hydroxyquinol; it also yields a monacetyl derivative. The author states that, besides the hydroxyl group, it contains two methoxy-groups, and is probably dimethylæsculetic acid. J. J. S.

Compounds from Lichens. By OSWALD HESSE (*Ber.*, 1897, 30, 357—366. Compare Abstr., 1895, i, 298, and Zopf, *ibid.*, 297 and

1896, i, 103).—Usnic acid, $C_{18}H_{16}O_7$, has been obtained from *Usnea barbata, U. longissima, Parmelia caperata, Cetraria pinastri, Cladonia rangiferina*, and *Placodium saxicolum*. The so-called β-usnic acid, and other similar acids obtained from these lichens, were mixtures of usnic acid with atranoric acid or atranorin.

Atranorin (Paternò and Oglialoro's atranoric acid) occurs in *Lecanora atra, L. sordida var. Swartzii, Cladonia rangiformis, Physcia parietina, Evernia prunastri, Parmelia perlata*, and other lichens; it is identical with parmelin. It appears to be the methylic salt, $C_{17}H_{15}O_6\cdot COOMe$, of an acid which could not be isolated, but for which the name of atranoric acid is proposed; when pure it melts at 187—188°. Heating with dilute acetic acid converts it into atranorinic acid, $C_{18}H_{18}O_9 + H_2O$ (not to be confused with Paternò's atranorinic acid), which melts when anhydrous at 157°. Paternò's atranorinic and atraric acids are no other than physciol, which is a phenol containing three oxygen atoms, and physcianin, which is methylic betorcinolcarboxylate; they are also formed when atranorin is heated with glacial acetic acid at 150°. The 'hæmatomminic,' 'hæmatommic,' and 'omminic' acids of Zopf, obtained by heating atranorin with methylic, ethylic, and isopropylic alcohols respectively, are better called the methylic, ethylic, and isopropylic salts of hæmatommic acid, which would have the formula $C_{10}H_9O_4\cdot COOH$; methylphysciol, melting at 142°, however, is formed in small amount at the same time, when it is the ethylic salt that is being prepared.

Chrysocetraric acid has again been prepared from *Cetraria pinastri*, and is now found to melt at 198°. Its composition, and that of its potassium, barium, calcium, lead, and copper salts, and of its acetyl derivative, agree with the formula $C_{18}H_{11}O_5\cdot OMe$. In the mother liquor from this acid, *cetrapic acid*, $C_{17}H_9O_5\cdot OMe$, is found together with usnic acid; it is a yellow substance melting at 147°, and forms a yellow *potassium salt*, $C_{18}H_{11}O_6K + H_2O$, and an *acetyl* derivative which melts at 155°. Cetrapic acid and its acetyl derivative greatly resemble vulpic acid and its acetyl derivative, both in melting point and in other properties, and just as the latter are converted into pulvic acid when hydrolysed, so the former yield a similar acid under the same circumstances. *Cetraria pinastri* contains 1·8 per cent. of these acids; of this amount, one-fourth is cetrapic, one-third chrysocetraric, and the rest usnic acid.

The author further confirms Zopf's statement that *Rhizocarpon geographicum var. lecanorinum* contains rhizocarpic acid together with psoromic acid; the latter acid, however, he finds to be identical with Schunck's parellic acid. Rhizocarpic acid is partially hydrolysed by aqueous sodium carbonate in the cold, yielding yellow *rhizocarpinic acid*, which melts at 170°; when warmed with alkalis, it yields the same substance as vulpic acid does under similar circumstances. The material at the author's disposal did not enable him to execute any analyses, but he is inclined to regard rhizocarpic acid as ethyldipulvic acid, $C_{40}H_{30}O_9$, assigning the formula $C_{38}H_{26}O_9$ to rhizocarpinic acid.

The following are some other acids which he has obtained from various lichens: *Divaricatic acid*, $C_{21}H_{23}O\cdot OMe$, melting at 129°, from

Evernia divaricata. *Ramalic acid*, $C_{16}H_{13}O_6 \cdot OMe$, melting at 179°, from *Ramalina pollinaria*, in which it occurs together with its isomeride evernic acid. *Sordidic acid*, $C_9H_{10}O_4 + \frac{1}{2}H_2O$, melting when anhydrous at 172°, with evolution of carbonic anhydride, from *Lecanora sordida var. rugosa*. *Thiophanic acid*, $C_{12}H_6O_{12} + H_2O$, melting when anhydrous at 242°, from *Lecanora sordida var. Swartzii*; it is yellow, yields a yellow *potassium salt*, $C_{12}H_3O_{12}K_3 + 8H_2O$, and is converted by strong hydriodic acid into thiophaninic acid, $C_{12}H_6O_9 + H_2O$, which melts when anhydrous at 264°; it is isomeric with mellitic acid, but gives a greenish-black coloration with ferric chloride. The same lichen yields *lecasteric acid*, $C_{10}H_{20}O_4$, melting at 116°, together with its *anhydride*, $C_{10}H_{18}O_3$, which melts at 105°, and is converted into the acid by aqueous sodium carbonate. *Caperatic acid*, $C_{21}H_{35}O_7 \cdot OMe$, melting at 132°, from *Parmelia caperata*, in which it occurs together with usnic acid and two substances, *caperin* and *caperidin*, which probably both have the formula $C_{24}H_{40}O_2$, and melt respectively at 243° and 262°.

Physcion, $C_{16}H_{12}O_5$ (Rochleder and Heldt's chrysophanic acid), has been obtained from *Gasparrisnia elegans* (= *Squamaria elegans*), *G. murorum*, and *Candelaria concolor*, in all of which it is the only crystallisable constituent. Neither chrysophanic acid proper (the acid of Chinese rhubarb) nor emodin has yet been found by the author in any lichen.

C. F. B.

Relations of the Azonium Bases to the Safranines. By OTTO FISCHER and EDUARD HEPP (*Ber.*, 1897, 30, 391—402. Compare Abstr., 1893, i, 282—283).—*Methylnaphthaphenazonium chloride*,

$$C_{10}H_6 <\begin{matrix} NMeI \\ | \\ N \end{matrix}> C_6H_4,$$

crystallises with $1H_2O$ in fan-shaped groups of brownish-yellow needles; the *nitrate* forms long, brownish-red prisms, and the *chromate*, *aurochloride*, and *platinochloride* are sparingly soluble yellow compounds. The *bromide*, prepared by heating naphthophenazine with methylic bromide, crystallises in concentric groups of orange-coloured needles.

n-Methylrosinduline, $NH:C_{10}H_5 <\begin{matrix} N \\ NMe \end{matrix}> C_6H_4$, is obtained in the form of its hydrochloride when naphthophenazonium chloride is treated with alcoholic ammonia. The free base crystallises in prisms with a bronze lustre, and gradually decomposes at 100°; it dissolves in sulphuric acid, forming a green solution, which becomes yellowish-red on dilution. The *hydrochloride* crystallises in dark red needles, readily soluble in water; the *nitrate*, *hydriodide*, *platinochloride*, and *aurochloride* have all been prepared.

n-Methylrosindone, $O:C_{10}H_5 <\begin{matrix} N \\ NMe \end{matrix}> C_6H_4$, formed when methylrosinduline is heated with dilute sulphuric acid, crystallises in matted, brick-red needles, which have a golden lustre; it gradually decomposes when heated, even at 100°. It dissolves in sulphuric acid with a cherry-red coloration.

Safraninone (*sym*-amidobenzeneindone), $O:C_6H_3 <\begin{matrix} N \\ NPh \end{matrix}> C_6H \cdot NH_2$,

is best prepared by heating phenosafranine hydrochloride with water and sodium acetate at 150°. It is soluble in water, can be diazotised, and forms condensation products with aldehydes. The salicylaldehyde *derivative*, $C_{25}H_{17}N_3O_2$, forms brown crystals with a bluish lustre. When safraninone is heated with dilute alkalis under pressure, safranol is formed. Acetic anhydride converts safraninone or its hydrochloride into a *monacetyl* derivative, which crystallises in slender, red needles melting above 280°, the *hydrochloride* of which forms compact, yellowish-red crystals; under no circumstances is a diacetyl derivative formed.

Safranol, $O{:}C_6H_3{<}\genfrac{}{}{0pt}{}{N}{NPh}{>}C_6H_3{\cdot}OH$, contains only one hydroxyl group, and yields a monethylic ether when heated with potash and ethylic iodide. The *hydrochloride* crystallises in plates which have a blue iridescence; it is sparingly soluble in hydrochloric acid, and is dissociated by water. *Acetylsafranol* crystallises in red prisms which have a greenish lustre and melt at 265—268°. *Methylphenosafranine*, $NMe{:}C_6H_3{<}\genfrac{}{}{0pt}{}{N}{NPh}{>}C_6H_3NH_2$, is obtained by the simultaneous oxidation of a mixture of paramethylphenylenediamine and two molecular proportions of aniline. It contains a primary amido-group, and only yields a *monacetyl* derivative, the *hydrochloride* of which forms red crystals with a faint green lustre and is sparingly soluble in alcohol.

These results show that the formulæ proposed by Kehrmann (Abstr., this vol., i, 107) and by Nietzki (this vol., i, 108) for the safranine derivatives cannot be correct, since, according to these, safraninone, safranol, and methylphenosafranine should all yield diacetyl derivatives. The normal safranine salts, moreover, are not to be looked on as azonium salts.

A. H.

Constitution of Tartrazine. By Richard Anschütz (*Annalen*, 1896, **294**, 219—243).—The tartrazines are the products of condensation of aromatic hydrazinesulphonic acids with dihydroxytartaric acid, and have been hitherto regarded as osazones; the author, however, adduces evidence in favour of representing them as pyrazolone derivatives, the colouring matter, tartrazine, being the sodium salt of parasulphophenylparasulphophenylhydrazonopyrazolonecarboxylic acid, $\genfrac{}{}{0pt}{}{N\!=\!=\!=\!=C(COONa)}{N(C_6H_4{\cdot}SO_3Na){\cdot}CO}{>}C{:}N{\cdot}NH{\cdot}C_6H_4{\cdot}SO_3Na$. The nomenclature is simplified by referring to this substance as the trisodium salt of *tartrazinic acid*, and parasulphophenylpyrazolonecarboxylic acid $\genfrac{}{}{0pt}{}{N\!=\!=\!=\!=C(COOH)}{N(C_6H_4{\cdot}SO_3Na){\cdot}CO}{>}CH_2$, is called *tartrazinogensulphonic acid*.

Sodium tartrazinate (tartrazine) is obtained by the condensation of phenylhydrazineparasulphonic acid (2 mols.) with dihydroxytartaric acid (1 mol.); its *hydrogen disodium* salt crystallises in small, bright yellow needles on adding sufficient hydrochloric acid to replace one atomic proportion of sodium; *barium tartrazinate* contains $6H_2O$, and forms deep orange-coloured crystals, whilst the *hydrogen barium* salt is anhydrous, and dissolves with difficulty in water.

Sodium ethylic tartrazinogensulphonate, $\genfrac{}{}{0pt}{}{N \overline{\qquad\quad} C(COOEt)}{N(C_6H_4\cdot SO_3Na)\cdot CO}>CH_2$, is the final product of the action of sodium phenylhydrazineparasulphonate on ethylic oxalacetate, and separates from water as a colourless, crystalline powder; the aqueous solution is acid, and develops a dark violet coloration with ferric chloride. *Silver ethylic tartrazinogensulphonate* forms small, white crystals indifferent towards air and light, and is sparingly soluble in cold water; the *barium* salt is amorphous, and dissolves with difficulty in cold water.

Sodium hydrogen tartrazinogensulphonate, $\genfrac{}{}{0pt}{}{N \overline{\qquad\quad} C(COOH)}{N(C_6H_4\cdot SO_3Na)\cdot CO}>CH_2$, is obtained by heating the sodium ethylic salt with caustic soda (2 mols.) on the water bath, and treating the liquid with excess of dilute hydrochloric acid; it is almost insoluble in cold water, crystallising in microscopic needles, and develops a violet coloration with ferric chloride. *Silver hydrogen tartrazinogensulphonate* crystallises in colourless prisms, and dissolves with great difficulty in cold water; *barium hydrogen tartrazinogensulphonate* is also crystalline.

Disodium ethylic tartrazinate is produced when diazotised sulphanilic acid is added to sodium ethylic tartrazinogensulphonate, and dissolves with difficulty in cold water; *barium ethylic tartrazinate* is dark yellow, and dissolves sparingly in hot water.

Diphenylizindihydroxytartaric acid,

$$COOH\cdot C(:N\cdot NHPh)\cdot C(:N\cdot NHPh)\cdot COOH,$$

the osazone of dihydroxytartaric acid, was obtained by Ziegler and Locher (Abstr., 1887, 578), and converted by Knorr into phenylhydrazoneketophenylpyrazolonecarboxylic acid (Abstr., 1888, 724); the former investigators observed that the ammonium salt is somewhat unstable, and on exposure to air yields a deep yellow substance which they regarded as a hydrogen ammonium salt. When the solution of this salt is heated, sparingly soluble, dark red needles are precipitated, and on treating the cold solution with silver nitrate, a dark red substance is formed which acquires a beautiful, cinnabar-red colour on exposure to light; the author finds that these compounds are not hydrogen ammonium diphenylizindihydroxytartrate and silver diphenylizindihydroxytartrimide, as supposed by Ziegler and Locher, but constitute the ammonium and silver salts respectively of Knorr's phenylhydrazoneketophenylpyrazolonecarboxylic acid (compare Wislicenus and Scheidt, Abstr., 1892, 458). M. O. F.

Bases in Fusel Oil. By EUGEN BAMBERGER and ALFRED EINHORN (*Ber.*, 1897, **30**, 224—229).—The authors have established the presence of pyridine and 2 : 5-dimethylpyrazine in fusel oil, and these bases also occur in commercial "pure amylic alcohol"; so that when this solvent is employed in effecting reduction with sodium, piperidine and 2 : 5-dimethylpiperazine are among the products. M. O. F.

Caffeidinecarboxylic Acid. By EMIL FISCHER and OTTO BROMBERG (*Ber.*, 1897, **30**, 219—221).—Caffeidinecarboxylic acid (compare Maly and Andreasch, Abstr., 1883, 1016) crystallises from acetone in long, colourless, prismatic needles, and melts at 160°, when it becomes red,

and evolves gas. On heating the acid with phosphorus oxychloride for 3 hours at 115°, caffeine is regenerated. M. O. F.

Methyl-ψ-morphine and its relation to ψ-Morphine and Morphine. By EDUARD VONGERICHTEN (*Annalen*, 1896, **294**, 206—219).—Although it has long been known that morphine is converted into ψ-morphine under the influence of oxidising agents in neutral or alkaline solution, the analogous change does not take place when codeine, the methyl ether of morphine, is submitted to the same treatment; this indifference is also exhibited by diacetylmorphine and methylmorphimethine. By the action of methylic iodide and caustic potash on ψ-morphine, the author has obtained methyl-ψ-morphine, instead of dimethy-ψ-morphine, or ψ-codeïne; as methyl-ψ-morphine contains three hydroxylic groups, the formula ascribed to the tetracetyl derivative of ψ-morphine by Hesse and Dankwortt receives confirmation, and fresh support is given to the view that ψ-morphine arises from the coalescence of two molecules of morphine with elimination of two atoms of hydrogen.

Methyl-ψ-morphine $C_{35}H_{38}N_2O_6$, is obtained in crystals containing $7H_2O$ when ψ-morphine is heated with dilute methylic alcohol, caustic soda and methylic iodide in a reflux apparatus on the water-bath; it is insoluble in hot water, alcohol, dilute caustic soda, ether, and chloroform, becomes anhydrous at 140°, then being very hygroscopic, and blackens at 257—260°. The *hydrochloride* crystallises in colourless, lustrous leaflets containing $4H_2O$; the *platinochloride* is yellow, and the *sulphate* crystallises in white needles which effloresce in the air. The *dimethiodide*, $C_{35}H_{38}N_2O_6,2MeI$, crystallises in prisms, and contains $4H_2O$; ammonia converts this substance into the *basic iodide*,

$$C_{35}H_{38}N_2O_6,MeI,MeOH,$$

which crystallises from hot water in lustrous leaflets containing $6H_2O$. Methyl-ψ-morphine is distinguished from ψ-morphine by its insolubility in cold, normal, caustic soda, which readily dissolves the latter base, the quantity of alkali sufficient for this purpose being less than the amount required on the assumption that ψ-morphine contains two phenolic hydroxyl groups. Whilst morphine combines readily with 1:2:4-chlorodinitrobenzene, yielding dinitrophenylmorphine, ψ-morphine remains almost entirely indifferent towards that agent.

Benzoic chloride converts morphine into the amorphous benzoyl derivative described by Beckett and Wright, ψ-morphine yielding a mixture of the dibenzoyl and tribenzoyl derivatives; the *tribenzoyl* derivative of methyl-ψ-morphine is amorphous, and the *hydrochloride* crystallises in long needles. The *triacetyl* derivative dissolves with difficulty in ether, and the *hydrochloride* crystallises from water in white needles; the *platinochloride* is yellow.

From the indifference of morphine derivatives towards oxidising agents, it is evident that the production of ψ-morphine from morphine depends on the phenolic hydroxyl group of the latter base remaining unsubstituted. M. O. F.

Organic Chemistry.

Conversion of Nitrites into Cyanides. By WILHELM KERP (*Ber.*, 1897, **30**, 610—612).—When sodium nitrite is heated with sodium acetate, the mixture explodes. If, however, the mass be mixed with anhydrous sodium carbonate and then heated, it glows and becomes dark-coloured, evolving hydrogen cyanide; it is then found to contain sodium cyanide, formed according to the equation, $CH_3 \cdot COONa + NaNO_2 = NaHCO_3 + NaCN + H_2O$. About 25 per cent. of the theoretical amount is obtained. Sodium nitrite, when heated with sodium formate, yields nothing but sodium carbonate, whereas with sodium propionate, it deflagrates, and forms small amounts of cyanide. When sodium acetate is heated with potassium nitrate, a violent explosion occurs, and cyanide and cyanate are formed, the same being the case with cream of tartar; in these cases, the formation of cyanide is probably due to the nitrite which is first formed. It appears probable that the first product of the action of the nitrite on sodium acetate is sodium nitrosoacetate, which then decomposes into hydrogen cyanide and sodium hydrogen carbonate: $NO \cdot CH_2 \cdot COONa = HCN + NaHCO_3$.

A. H.

Formation of Diacetylenyl (Butadiine) from Copper Acetylene. By ARTHUR A. NOYES and C. W. TUCKER (*Amer. Chem. J.*, 1897, **19**, 123—128).—Reboul (*Compt. rend.*, **54**, 1229), on passing acetylene into bromine, noticed the formation of a crystalline substance, and Sabanéeff (*Annalen*, **178**, 114) who further investigated this substance, ascribed to it the formula, $C_4H_2Br_6$, and believed it to be hexabromotetramethylene. The authors find that, if pure acetylene, generated from calcium carbide, be passed into boiling bromine, no trace of the solid substance is produced, the true explanation of its origin being that when copper acetylide, made by passing acetylene into ammoniacal cuprous chloride till saturated, is used for generating acetylene, cupric chloride is formed, and this exerts an oxidising action. The hydrocarbon forming the bromide is therefore an oxidation product of acetylene or its copper compound, as represented by the following equations. $2C_2Cu_2 + 2CuCl_2 = C_4Cu_2 + 2Cu_2Cl_2$. $C_4Cu_2 + 2HCl = CH⋮C \cdot C⋮CH + Cu_2Cl_2$. By analysis, and from the determination of its molecular weight by the boiling point method, the substance is proved to have the formula $C_4H_2Br_6$, and is the hexabromide of the unsaturated hydrocarbon diacetylene (diacetylenyl, butadiine). It crystallises in colourless, transparent, orthorhombic plates, melts at 183·5° (corr.), and evolves bromine when heated above its melting point, whilst at 220°, under a pressure of 40 mm., a liquid distils over which partially recombines with the bromine vapour to form the original solid substance.

A. W. C.

Action of Hydrogen Bromide on Methylbutallylcarbinol. By MAX SCHRAMM (*Ber.*, 1897, **30**, 636—638).—When methylbutallyl-

carbinol, $CH_2:CH\cdot CH_2\cdot CH_2\cdot CHMe\cdot OH$, is saturated at 0° with hydrogen bromide, and heated at 70° in closed vessels for 4 hours, a colourless oil is obtained having the odour of oranges; it boils for the most part at 205—211°, and has the composition $C_6H_{12}Br_2$. The substance is probably 2 : 5-dibromohexane, which, according to Demjanoff, boils at 210°; the product from methylbutallylcarbinol, however, is not free from admixture, as it does not solidify at the temperature of the air, although 2 : 5-dibromohexane melts at 38—39°.

Alcoholic potash converts 2 : 5-dibromohexane into $\Delta_{2,4}$-hexinene (2 : 4-hexadiene), a colourless, mobile liquid which boils at 87—89°; this substance is described by Griner as occurring in two modifications, boiling at 77—82° and 82—83° respectively. On adding bromine to a solution of 2 : 4-hexadiene in chloroform, 2 : 3 : 4 : 5-tetrabromohexane is produced; it crystallises in slender, white needles having a faint, camphor-like odour, and melts at 180·5—181°. M. O. F.

Cyclic Ethers of Polyatomic Alcohols. By CARL STOEHR (*J. pr. Chem.*, 1897, [ii], 55, 78—94).—When glycerol is distilled with ammonium phosphate or phosphoric acid, an ether is formed which has a composition and molecular weight corresponding with the formula $C_6H_{10}O_3$; it crystallises from ether in colourless, lustrous tablets, melts at 124—125°, and boils at 209° (corr.). This compound does not appear to contain either the hydroxyl or the carbonyl group, and is very stable towards oxidising agents. With bromine, it combines to form an *additive* compound, which crystallises in red needles and loses bromine over sulphuric acid, leaving the unaltered ether. It also forms, with mercuric chloride, a *compound*, $C_6H_{10}O_3,HgCl_2$, which is sparingly soluble in cold water, and crystallises in thin, lustrous plates melting at 223°. This ether appears therefore to be formed from 2 mols. of glycerol, with the loss of 3 mols. of water. A compound of this character may, however, be formed in several different ways, and its exact constitution has not yet been determined.

When glycerol is distilled with ammonium phosphate and ammonium chloride, or when it is distilled in a current of hydrogen chloride, a substance of the molecular formula $C_6H_{10}O_2Cl_2$ is produced, which is apparently identical with a compound previously obtained by Fauconnier and Sanson (Abstr., 1888, 244). This compound, which the author provisionally names *di-epichlorhydrin*, crystallises in vitreous, monosymmetric prisms, melts at 112—113°, and boils at 232—233°. The chlorine atoms readily undergo displacement, whereas the oxygen atoms appear to be very firmly combined. When the compound is heated with alcoholic potassium iodide at 150°, it yields the corresponding *di-epiiodhydrin*, which crystallises in colourless, brittle needles, melts at 160°, and can be sublimed without decomposition, but decomposes when distilled. Aqueous ammonia converts it into *di-epihydrinamide*, $C_6H_{10}O_2(NH_2)_2$, which is a strong diacid, diprimary base. It boils at 255—256° (uncorr.), almost without decomposition, and crystallises from water in lustrous, monosymmetric tablets, which contain water of crystallisation. It absorbs carbonic anhydride when exposed to the air, and forms crystalline salts. The *hydrochloride* is readily soluble in water; the *platinochloride* crystallises with $2H_2O$; the compound with *mercuric*

chloride decomposes at 287—288°; the *picrate* decomposes at 260—261°. The *dibenzoyl* derivative crystallises in lustrous, colourless plates, melting at 229°. Nitrous acid converts the base into a dihydroxyl derivative, which has not yet been closely examined.

Di-epichlorhydrin, like the glycerol ether, forms an unstable *additive* compound with bromine, and does not appear to contain either hydroxyl or carbonyl groups. The formula is probably

$$CH_2Cl\cdot CH\begin{matrix}<\end{matrix}\begin{matrix}O\cdot CH_2\\CH_2\cdot O\end{matrix}\begin{matrix}>\end{matrix}CH\cdot CH_2Cl.$$

A. H.

Amount of Pentosan in Cotton Wool. By H. SURINGAR and BERNHARD TOLLENS (*Zeit. angw. Chem.*, 1897, 4—5).—The authors find that cotton wool, when boiled with dilute (4 per cent.) sulphuric acid for 8 hours, yields a certain quantity of sugar, chiefly dextrose. The syrup did not give any definite reaction with phloroglucinol and hydrochloric acid, and they consequently conclude that cotton wool contains but mere traces of pentosans, if any.

L. DE K.

Solubility of Cane-Sugar in Dilute Alcohol. By SCHREFELD (*Zeit. anal. Chem.*, 1897, **36**, 196—197; from *Zeit. Zucker. Ind*, **44**, 971).—A table giving the number of grams of sugar, dissolved at 14° by 100 c.c. of a mixture of alcohol and water, for every increment of 5 per cent. of alcohol in the solvent.

M. J. S.

Brominated Bases of the Fatty Series. By ALFRED PARTHEIL and H. VON BROICH (*Ber.*, 1897, **30**, 618—621).—Paal (Abstr., 1892, 30) has stated that the trimethyltrimethinammonium bromide, which is formed by the action of alcoholic potash on dibromopropyltrimethylammonium bromide, is in reality a propargyl derivative; this the authors consider to be improbable, because when trimethyltrimethinammonium hydroxide is heated, trimethylamine is formed, along with a second substance which is not propargylic alcohol, but of which the actual constitution has not yet been decided. Trimethyltrimethinammonium hydroxide can be distilled under a low pressure almost without decomposition. It yields a *platinochloride*, $(C_3H_3\cdot NMe_3)_2PtCl_6$, which crystallises in slender, brownish-red needles. The *picrate* is sparingly soluble.

Although an attempt to synthesise trimethyltrimethinammonium bromide proved unsuccessful, the following substances were obtained in the course of the experiments. Allylic bromide reacts with 2 mols. methylamine in aqueous solution to form the *hydrobromide* of *methyldiallylamine*, a base which boils at 112°. By the action of methylic iodide on allylamine, *methylallylamine* is obtained as a mobile liquid, boiling at 64—66°. The *nitroso*-compound is a yellow oil which boils at 170—174°. The *platinochloride*, $(C_3H_5\cdot NHMe)_2,H_2PtCl_6$, melts at 164°. *Methyldibromopropylammonium bromide*, $C_3H_5Br_2\cdot NH_2MeBr$, crystallises in colourless prisms, which melt at 179°. The corresponding *platinochloride* is a crystalline precipitate, and the *aurochloride* forms yellow crystals.

Dimethylallylamine, $C_3H_5\cdot NMe_2$, is formed by the action of allylic bromide on dimethylamine in alcoholic solution. The *platinochloride*

forms reddish-brown crystals. *Dimethyldibromopropylammonium bromide*, $C_3H_5Br_2\cdot NMe_2HBr$, melts and decomposes at 188—189°. The *chloride* decomposes at 185°; the *platinochloride* forms yellow crystals, and the *aurochloride* reddish-yellow crystals. No definite product of the action of alcoholic potash on the bromide could be isolated.

Allylic bromide unites with triethylamine to form an additive compound, and this combines with bromine to form a *perbromide*,

$$C_3H_5Br_2\cdot NEt_3Br,Br_2,$$

crystallising in reddish-brown needles. On reduction with alcohol, this yields *triethyldibromopropylammonium bromide*, $C_3H_5Br_2\cdot NEt_3Br$, which crystallises in long, hygroscopic needles; the *platinochloride* melts and decomposes at 228—230°; the *aurochloride* is almost insoluble in water. One molecule of alcoholic potash converts the bromide into *triethylmonobromallylammonium bromide*, $C_3H_4Br\cdot NEt_3Br$; this forms white, hygroscopic crystals, and yields a *platinochloride*, which separates in yellowish-red crystals. Two molecules of alcoholic potash, on the other hand, convert the bromide into *triethyltrimethinammonium bromide*, $C_3H_3\cdot NEt_3Br$, which is a white, crystalline powder; the corresponding *platinochloride* is crystalline. A. H.

Behaviour of Diazomethane towards Nitramines. By OTTO DEGNER and HANS VON PECHMANN (*Ber.*, 1897, **30**, 646—654. Compare Abstr., 1895, i, 493).—The value of diazomethane in determining the structure of tautomeric substances (*loc. cit.*) suggests its employment in attacking the question of the constitution of nitramines. Although, from previous experience of this class of compounds, the production of oxygen ethers might be anticipated, the result is largely influenced by the nature of the complex with which the nitramine group is linked; thus, whilst phenylnitramine yields the oxygen ether almost exclusively, the nitrogen ether preponderates in the case of methylnitramine, nitrocarbamide, and others, nitramide yielding equal quantities of nitrogen and oxygen ethers.

Carbamide is indifferent towards diazomethane, but this agent resolves nitrocarbamide into isocyanic acid and nitramide, according to the equation $O{:}C(NH_2)\cdot NH\cdot NO_2 = O{:}C{:}NH + NH_2\cdot NO_2$, the products being at once converted into the respective methyl derivatives; diazomethane and nitrocarbamide are brought together in ethereal solution, and when the action is at an end, the medium is distilled off at the lowest possible temperature. The ethereal distillate, which has an intense, irritating odour, is without action on Fehling's solution, and does not give the nitramine reaction; it may be shown to contain methylcarbimide by its behaviour towards phenylhydrazine, aniline, and ammonia. The residue contains methylnitramine and dimethylnitramine, along with the oxygen methyl ether of the former (this vol., i, 8).

Methylphenylsemicarbazide, $NHMe\cdot CO\cdot NH\cdot NHPh$, separates in lustrous leaflets when petroleum is added to a mixture of the ethereal distillate with phenylhydrazine; it softens at 148°, and melts at 154—155°. The solution in concentrated sulphuric acid becomes violet with ferric chloride, and the aqueous solution develops a bluish-black coloration with Fehling's solution, the latter being completely reduced on gently heating; nitric acid gives rise to a yellow, crystalline *nitroso*-derivative,

and concentrated hydrochloric acid in sealed tubes at 100° resolves the substance into carbonic anhydride, methylamine, and phenylhydrazine.

Methylamidocarbonylazobenzene, NHMe·CO·N:NPh, is obtained by oxidising methylphenylsemicarbazide in chloroform with mercuric oxide; it crystallises from boiling petroleum in beautiful, long, red needles, and melts at 86°.

Symmetrical phenylmethylcarbamide, NHMe·CO·NHPh, is produced when the ethereal solution of methylcarbimide is mixed with aniline and petroleum added; it crystallises from hot water in colourless, lustrous leaflets, and melts at 149—150°. Potassium dichromate added to the solution in concentrated sulphuric acid develops a violet coloration; concentrated hydrochloric acid at 150° resolves it into carbonic anhydride, methylamine, and aniline; *symmetrical parabromophenylmethylcarbamide* crystallises in long, silky needles, and melts at 212°.

When dry ammonia gas is passed into the ethereal solution of methylcarbimide, methylcarbamide is precipitated. Water or alkali carbonates convert the salt into dimethylcarbamide.

Symmetrical methylnitrocarbamide, NHMe·CO·NH·NO_2, occurs in the residual oil from which the ethereal solution of methylcarbimide has been distilled; it crystallises from benzene in needles, and melts at 105—106°. Concentrated sulphuric acid decomposes the substance, liberating gas, and ferrous sulphate and sulphuric acid give the nitrosamine reaction; hot potassium carbonate solution liberates methylamine. The *potassium* derivative forms colourless needles, and melts, decomposing at 145°; the *mercuric* derivative is insoluble in water.

Asymmetrical methylnitrocarbamide, NH_2·CO·NMe·NO_2, obtained by nitrating methylcarbamide, crystallises from benzene in colourless needles, and melts and evolves gas at 156—157° (compare Thiele and Lachmann, Abstr., 1896, i, 207). The *potassium* derivative crystallises in colourless needles, melting and decomposing at 160°, and the *silver* and *ammonium* derivatives are definite.

It is remarkable that, whilst nitration of ethylcarbamide should give rise to symmetrical ethylnitrocarbamide, as shown by Thiele and Lachmann, the asymmetrical compound should be obtained from methylcarbamide. M. O. F.

Some Metallic Derivatives of Dithioacetylacetone. By VICTOR VAILLANT (*Bull. Soc. Chim.*, [iii], **15**, 514—519).—In a previous paper (Abstr., 1895, i, 168), it was shown that when an ethereal solution of dithioacetylacetone, $C_{10}H_{14}S_2O_4$, is treated with sodium, hydrogen is evolved and the compound $C_{10}H_{12}Na_2S_2O_4$ is formed; this substance can, however, be obtained more easily by the action of sodium ethoxide on the ethereal solution of dithioacetylacetone, of which the formula is probably $S_2(CHAc_2)_2$. This sodium derivative can be obtained in yellow needles by crystallisation from alcohol or water, but is insoluble in benzene and ether. It decomposes when heated to 150°, or if its solution is boiled. It is alkaline to phenolphthalein.

The *potassium* derivative resembles the sodium compound. The *magnesium* derivative, $C_{10}H_{12}S_2O_4Mg$, a yellow, crystalline powder, is obtained by the action of an alkaline solution of dithioacetylacetone

on a solution of a magnesium salt. The *cobalt* derivative, $C_{10}H_{12}S_2O_4Co$, a rose-coloured salt crystallising in octahedra, is obtained by the same process. It is insoluble in water, but soluble in hot alcohol. The *nickel* derivative, $C_{10}H_{12}S_2O_4Ni$, forms pale green crystals belonging to the quadratic system; it is very soluble in alcohol, but insoluble in water. The copper derivative, $C_{10}H_{12}S_2O_4Cu$ (see Abstr., 1895, i, 168), which is most easily obtained by treating an ethereal solution of dithioacetylacetone with copper acetate, forms bright green crystals, insoluble in water and alcohol, but soluble in chloroform. The *ferric* derivative $(C_{10}H_{12}S_2O_4)_3Fe_2$, obtained by double decomposition, forms minute, deep red crystals, insoluble in water, slightly soluble in alcohol, and very soluble in chloroform. The *aluminium* derivative, $(C_{10}H_{12}S_2O_4)_3Al_2$, forms minute, yellowish-white crystals. Its method of preparation and properties agree with those of the ferric salt. The *uranium* derivative, $C_{10}H_{12}S_2O_4UO_2$, can be obtained by double decomposition, or by shaking a solution of uranium acetate with a chloroform solution of dithioacetylacetone. It crystallises from alcohol in yellow plates. The *bismuth* derivative is a yellow powder, and the *manganese* derivative is a white powder. M. W. T.

The Specific Gravities of Aqueous Solutions of Formic Acid. By GEORGE M. RICHARDSON and PIERRE ALLAIRE (*Amer. Chem. J.*, 1897, **19**, 149—151).—The authors have determined the specific gravities of mixtures of formic acid and water, and give a table calculated from the results of their observations for every unit by weight of formic acid from 1—100. A. W. C.

Oxidation of the Acids Derived from Fats. By THEOD. MARIE (*Bull. Soc. Chim.*, 1896, [iii], **15**, 508—510).—The author shows that normal valeric acid is one of the products of the oxidation of stearic acid by potassium permanganate. M. W. T.

Chlorides, Amides, and Nitriles of Cerotic and Melissic Acids. By THEOD. MARIE (*Bull. Soc. Chim.*, 1896, [iii], **15**, 503—508).—*Cerotic chloride*, obtained by the action of phosphorus pentachloride on the acid, melts at 47°, and reacts readily with water. In order to prepare *cerotamide*, the mixture of cerotic chloride and phosphorus oxychloride is poured, while warm, into ammonia. The amide is soluble in alcohol, but insoluble in ether and water; it melts at 106°. *Cerotonitrile*, obtained by heating the corresponding amide with phosphoric anhydride, is a white, crystalline substance, soluble in alcohol, benzene, ether, &c., but insoluble in water; it melts at 58°.

Melissic chloride, which can be obtained by the same process as cerotic chloride, melts at 60°; *melissamide* melts at 116°, and *melissonitrile* at 70°. These substances closely resemble the corresponding derivatives of cerotic acid. M. W. T.

Condensation of Acetone with Ethylic Acetoacetate. By HERMANN PAULY (*Ber.*, 1897, **30**, 481—485).—When a mixture of acetone and ethylic acetoacetate is saturated with hydrogen chloride in the cold, and allowed to remain for a time, the product is found to consist of mesityl oxide, a little ethylic isodehydracetate and *ethylic isopropylidenea etoacetate*; the last-mentioned is a yellowish oil, of pleasant odour;

it does not solidify at $-20°$, and boils at 214—216° (uncorr.); its sp. gr. = 1·001 at 20°/4°. When heated with alkalis or dilute acids, it yields dimethylacrylic acid and acetic acid. Phenylhydrazine converts it into phenylmethylisopropylidenepyrazolone and isopropylidenebisphenylmethylpyrazolone (*Knorr*, Abstr., 1887, 601). A. H.

Substituted Amido-acids, and Imides of Asymmetric Dimethylsuccinic Acid. By WILHELM KERP (*Ber.*, 1897, **30**, 613—617).—In view of the fact that Auwers (Abstr., 1896, i, 640), has found the melting points of the anilic acids of asymmetric dimethylsuccinic acid to be about 20° higher than they had previously been found by the author (*Diss. Bonn.*, 1890), the latter has revised the work; and he now finds that the melting points of these substances cannot be exactly determined in the ordinary way, since water is lost during the process, and the temperature, which is observed, depends on the rate of heating, width of tube, &c. The anilic acid crystallises in lustrous plates, and melts at 169° when slowly heated, but at 185—186° if rapidly heated. The orthotolilic acid crystallises in small, lustrous scales, and melts at 146—147° or 154—155°. The paratolilic acid melts at 161—162° or 181° (Auwers 180—185°).

The properties of the anils corresponding with these acids are identical with those given by Auwers. A. H.

Formation of Carbon Chains. XIII. Diethyldisulphonemethane and Ethylic Diethoxymalonate. By CARL A. BISCHOFF (*Ber.*, 1897, **30**, 487—491. Compare Abstr., 1896, i, 600).—Diethylsulphonemethane behaves, in various reactions, in a different manner from ethylic malonate, which it resembles in structure, the group SO_2 replacing COO. Thus, when its potassium compound is treated with iodine, it simply forms an iodine substitution derivative, $CI_2(SO_2Et)_2$, and not an analogue of ethylic ethylenetetracarboxylate, $C_2(SO_2Et)_4$. When this di-iodo-derivative, moreover, is treated with ethylic sodiomalonate, it does not bring about the linking of two molecules of the ethylic malonate, but merely yields ethylic ethylenetetracarboxylate and regenerated diethylsulphonemethane. It has been shown by Crum Brown and Fairbairn (*Proc. Roy. Soc. Edinb.*, 1894—1895, 383), that sodium ethylic mercaptan behaves towards ethylic dibromomalonate in a somewhat similar manner, and the author finds that sodium ethoxide in this respect resembles the mercaptan, although, when ethylic dibromomalonate is treated with sodium methoxide, a very small amount of the normal product, *ethylic diethoxymalonate* is formed. This boils at 228°, and crystallises in large prisms melting at 43—44°. The configurations, $C(OEt)_2(COOEt)_2$ and $C(SEt)_2(COOEt)_2$, therefore, seem to be dynamically unfavourable, although ethylic diphenoxymalonate, $C(OPh)_2(COOEt)_2$, and ethylic diacetylmesoxalate $C(OAc)_2(COOEt)_2$, are readily produced. A. H.

Constitution of Caffeine, Xanthine, Hypoxanthine, and Allied Bases. By EMIL FISCHER (*Ber.*, 1897, **30**, 549—559).—In this paper, the author discusses the constitution of these bases, and considers that, owing to the large increase in the number of derivatives of xanthine

and hypoxanthine, the old system of nomenclature is no longer applicable. In his opinion, it is most convenient to consider all these compounds as derivatives of purine ($C_5N_4H_4$), and to number the atoms in its ring nucleus as follows $\begin{array}{l} \scriptstyle 1 \;\; 6 \;\; 5 \;\; 7 \\ N\cdot C\cdot C\cdot N \\ C\cdot N\cdot C\cdot N \\ \scriptstyle 2 \;\; 3 \;\; 4 \;\; 8 \end{array}\!\!>C_9$. Hypoxanthine is thus 6-oxypurine; uric acid = 2 : 6 : 8-trioxypurine; caffeine = 1 : 3 : 7-trimethyl-2 : 6-dioxypurine; hydroxycaffeine = 1 : 3 : 7-trimethyl-2 : 6 : 8-trioxypurine; guanine = 2-amido-6-oxypurine; adenine = 6-amidopurine. The function of the oxygen atoms, whether hydroxylic or ketonic, is purposely not indicated in the names, owing to the possibility of tautomeric forms existing. J. F. T.

New Synthesis of Uric Acid, Hydroxycaffeine, and Amidodioxypurine. By Emil Fischer (*Ber.*, 1897, **30**, 559—573. Compare Abstr., 1896, i, 12).—Fusion with oxalic acid converts ψ-uric acid into uric acid (*loc. cit.*), and this effect is also produced by the action of hot, dilute mineral acids; the latter method gives rise to a purer product in more remunerative yield, and is applicable to all substances typified by ψ-uric acid.

In order to obtain uric acid by this process, finely-powdered ψ-uric acid is heated with 500 parts of 20 per cent. hydrochloric acid for 15—20 minutes, the liquid being evaporated to one-fifteenth of its original volume, when uric acid crystallises from the solution. The production of 1 : 3-dimethyluric (γ-dimethyluric) acid from Techow's dimethyl-ψ-uric acid is effected in the same way.

7-Methyl-ψ-uric acid, $CO<\begin{matrix}NH\cdot CO\\NH\cdot CO\end{matrix}>CH\cdot NMe\cdot CO\cdot NH_2$, is obtained by the action of potassium cyanate on methyluramil, the latter being prepared by heating an aqueous solution of alloxan with methylamine sulphite for 3 hours at 70—75°, and saturating with hydrogen chloride the solution of methylamine methylthionurate thus produced; small quantities of uramil and ψ-uric acid occur as by-products in this change. The conversion of 7-methyl-ψ-uric acid into 7-methyluric acid is much more rapid than in the case of ψ-uric acid or the dimethyl derivative; a 1 per cent. solution of hydrochloric acid will bring about the change, which also proceeds slowly when an aqueous solution is heated at 100° in absence of acid. 3 : 7-Dimethyluric acid is conveniently prepared from 7-methyluric acid by heating the anhydrous lead derivative with ethereal methylic iodide for 12 hours at 170—175°; on dissolving the product in water, hydrogen sulphide liberates 3 : 7-dimethyluric acid from the solution.

1 : 3 : 7-*Trimethyluramil*, $CO<\begin{matrix}NMe\cdot CO\\NMe\cdot CO\end{matrix}>CH\cdot NHMe$, is prepared by heating dimethylalloxan with methylamine sulphite for 1 hour at 65—70°; when the two substances are mixed, a feeble, red coloration is developed, and after some time has elapsed, the solution deposits colourless, prismatic needles of the *additive compound*, $C_6N_2O_4H_6 + NH_2Me,H_2SO_3$. Trimethyluramil crystallises from water in colourless needles, and gradually decomposes when the aqueous solution is boiled;

the dry substance is, however, quite stable. It becomes red at 100°, and completely decomposes at about 200°.

1 : 3 : 7-*Trimethyl-ψ-uric acid*, $CO<\genfrac{}{}{0pt}{}{NMe\cdot CO}{NMe\cdot CO}>CH\cdot NMe\cdot CO\cdot NH_2$, obtained by treating trimethyluramil with an aqueous solution of potassium cyanate, crystallises from water in colourless prisms containing $1H_2O$, which is eliminated at 110°; when heated rapidly, it melts and decomposes at 195°, but if the temperature is slowly raised, decomposition occurs at 180—190°, the product remaining solid at 300°. Trimethyluramil is converted into hydroxycaffeine under the influence of a hot, 1 per cent. solution of hydrochloric acid, and when hydroxycaffeine is methylated, a mixture of methoxycaffeine and tetramethyluric acid is obtained; the latter substance melts at 223° (228° corrected), and not at 218°, as previously stated.

2-*Amido*-6 : 8-*dioxypurine*,
$NH_2\cdot C\leqslant\genfrac{}{}{0pt}{}{NH\cdot CO\cdot C\cdot NH}{N\text{———}C\cdot NH}>CO$ or $NH_2\cdot C\leqslant\genfrac{}{}{0pt}{}{N\cdot CO\cdot C\cdot NH}{NH\text{—}C\cdot NH}>CO$, is prepared from imido-ψ-uric acid (Traube, Abstr., 1894, i, 9) by the action of hydrochloric acid of sp. gr. = 1·19 in closed tubes at 120°; it dissolves with extreme difficulty in water, and decomposes without fusion at about 380°. The *sulphate*, and the *ammonium* derivative are decomposed on boiling their aqueous solutions; the *sodium* derivative forms colourless, microscopic needles, and the *barium* derivative dissolves with great difficulty in water. Hot nitric acid rapidly decomposes the substance, but the solution does not give the murexide reaction in a striking manner; chlorine converts amidodioxypurine into guanidine hydrochloride.

Amidodioxypurine is also produced when bromoguanine is treated with hydrochloric acid in sealed tubes at 130°. M. O. F.

Substituted Amides of Oxalic Acid. By WILHELM KERP and KARL UNGER (*Ber.*, 1897, **30**, 579—585).—Although amidoacetic acid has no action on ethylic cholate at the ordinary temperature, substituted amides of oxalic acid are readily obtained when the substance is brought into contact with ethylic oxalate, oxamethane, and ethylic oxamethaneacetate; ethylic amidoacetate also acts on the chloride of monethylic oxalate.

Oxalyldiglycocine (*oxamidediacetic acid*), $C_2O_2(NH\cdot CH_2\cdot COOH)_2$, is produced on adding ethylic oxalate (1 mol.) to an aqueous solution of potassium amidoacetate (2 mols.); it is somewhat soluble in boiling water, but dissolves sparingly in the cold agent, and is insoluble in common solvents. When rapidly heated, it melts and decomposes at 250°. The *silver* salt is colourless, and resists the action of light, and the *methylic* salt crystallises in lustrous, colourless leaflets, and melts at 138—140°. The *monethylic* salt is obtained by the action of potassium amidoacetate on ethylic oxamethaneacetate; it crystallises in slender, white needles, and melts at 164—165°.

Amido-oxalylglycocine (*oxamidoacetic acid*),
$$NH_2\cdot CO\cdot CO\cdot NH\cdot CH_2\cdot COOH,$$
is produced when potassium amidoacetate acts on oxamethane; it crystallises in colourless needles, becomes brown at 214°, and melts,

and decomposes at 224—228°. The *potassium* salt contains $2H_2O$, and the *silver* salt is colourless, and resists the action of light.

Ethylic oxamethaneacetate, $COOEt\cdot CO\cdot NH\cdot CH_2\cdot COOEt$, is obtained by heating the chloride of monethylic oxalate with ethylic amidoacetate hydrochloride suspended in dry benzene in a reflux apparatus; it is a colourless, viscous liquid, having the sp. gr. = 1·183 at 20°, and boils at 197—198° under a pressure of 12 mm.

Ethylic oxamethanepropionate, $COOEt\cdot CO\cdot NH\cdot CHMe\cdot COOEt$, is produced when the chloride of monethylic oxalate is heated with the hydrochloride of ethylic amidopropionate suspended in dry benzene in a reflux apparatus; it boils at 169—172° under a pressure of 14 mm.

M. O. F.

Semioxamazide. By WILHELM KERP and KARL UNGER (*Ber.*, 1897, 30, 585—593).—The readiness with which semicarbazide combines with aldehydes and ketones, coupled with the disadvantage offered by the agent in frequently giving rise to two modifications of semicarbazone, has led the authors to prepare semioxamazide, and study its behaviour towards the groups in question; whilst, however, aldehydes produce in quantitative yield semioxamazones which melt at definite temperatures, the action of semioxamazide on ketones is less general, and usually proceeds under certain limiting conditions.

Semioxamazide, $NH_2\cdot CO\cdot CO\cdot NH\cdot NH_2$, is obtained by gently heating oxamethane with an alcoholic solution of hydrazine on the water bath; it crystallises in slender, lustrous leaflets, and melts and decomposes at 220—221°. The substance dissolves readily in hot water, and sparingly in the cold agent, being insoluble in alcohol and ether; acids and alkalis dissolve it readily, and a cold solution of silver nitrate is immediately reduced. The *hydrochloride* is precipitated in long, slender, colourless needles on adding alcohol to the aqueous solution, and the *sulphate*, prepared in a similar manner, also crystallises in white needles. When a concentrated solution of copper chloride (1 mol.) is added to semioxamazide hydrochloride dissolved in the minimum quantity of water, a deep blue, crystalline *copper chloride* derivative, $NH_2\cdot CO\cdot CO\cdot N(CuCl)\cdot NH_2,HCl$, separates after a few days, associated with a green, pulverulent *copper* derivative, $(C_2O_2N_3H_4)_2Cu_2 + H_2O$. The *carbamide* crystallises from hot water in slender needles, and melts and decomposes at 215°. When semioxamazide is melted, or heated in sealed tubes for 2 hours at 145°, ammonia is liberated and two compounds are formed, one of which is a polymeride of cyanic acid; this substance probably has the constitution $\begin{matrix} CO\cdot NH \\ | \quad\;\; | \\ CO\cdot NH \end{matrix}$, and the compound associated with it is the ammonium derivative.

Benzaldehyde semioxamazone is a colourless, finely divided powder, almost insoluble in common solvents; it sublimes very readily in long threads, and melts at 264°, with slight evolution of gas.

Cinnamaldehyde semioxamazone is a white powder and sublimes in woolly needles; when rapidly heated, it melts and decomposes at 274°.

Salicylaldehyde semioxamazone crystallises from hot dilute alcohol in small, lustrous, pale yellow needles, and melts at 255°.

Citraldehyde semioxamazone is obtained as a white spongy mass,

insoluble in water and ether, but dissolving readily in alcohol; it melts at 190—191°.

Furfuraldehyde semioxamazone is a yellowish-white powder which becomes brown at 240°, sinters at 259°, and melts, decomposing, at 264°; when heated cautiously, it sublimes in small, yellowish-white needles. The insoluble character of this substance recommends its application in the estimation of those carbohydrates which yield furfuraldehyde on hydrolysis; quantitative experiments carried out in this direction have invariably led to satisfactory results.

Acetophenone semioxamazone crystallises from alcohol in long, lustrous, white needles; it melts at 214°.

Ethylic acetoacetate semioxamazone separates from alcohol in slender needles and melts at 125—127°.

Carvone semioxamazone crystallises in aggregates of snow-white needles and melts at 187—188°.

Methylhexanone semioxamazone slowly separates from a mixture of alcohol and ether in white needles and melts at 153—154°.

Menthone semioxamazone crystallises from alcohol in aggregates of white needles and melts at 177°. M. O. F.

Hagemann's Ethylic Methylcyclohexenonecarboxylates, and their Conversion into an Isomeride of Camphor. By JOHANN ANTON CALLENBACH (*Ber.*, 1897, **30**, 639—646. Compare Abstr., 1893, i, 393).—By the action of methylenic iodide on ethylic sodioacetoacetate, Hagemann obtained a mixture of two isomeric substances having the composition $C_{10}H_{14}O_3$, separable by treatment with dilute caustic soda, the acidic modification developing a deep red coloration with ferric chloride, towards which the neutral form is indifferent; the constitutional difference between the two isomerides is not of the character described by Hagemann (*loc. cit.*), the substances being tautomeric, and the structure of the acidic form is represented by the expression $CMe{<}{\begin{matrix}CH\cdot C(OH)\\CH_2—CH_2\end{matrix}}{>}C\cdot COOEt$, the ketonic modification of which formulates the neutral salt. This is shown by the complete conversion of the ketonic into the enolic form under the influence of sodium ethoxide, and by the production of a single isopropyl derivative from both salts; moreover, the sp. gr. = 1·0816 in both cases, and the enolic form has the refractive index $n_D = 1{\cdot}4859$, giving the molecular refraction 48·38, whilst the ketonic modification has the refractive index $n_D = 1{\cdot}4823$, and the molecular refraction 47·95.

Ethylic-3-methyl-6-isopropyl-Δ_2-cyclohexenone-6-carboxylate,

$$CMe{<}{\begin{matrix}CH—CO\\CH_2\cdot CH_2\end{matrix}}{>}CPr^{\beta}\cdot COOEt,$$

is obtained by the action of sodium ethoxide and isopropylic iodide both on the ketonic and on the enolic salts; it boils at 157—158° under a pressure of 18 mm., has the sp. gr. = 1·0646 at 17°, and the refractive index $n_D = 1{\cdot}4838$. *3-Methyl-6-isopropyl-Δ_2-cyclohexenonecarboxylic acid* crystallises from light petroleum, ether, or benzene in beautiful, transparent prisms melting at 119—120°, and dissolves readily in water; the *silver* salt crystallises from water in long, colourless, transparent needles, and resists the action of light.

When the foregoing acid is distilled, carbonic anhydride is eliminated, and the *ketone*, $CMe{<}\begin{smallmatrix}CH\text{—}CO\\CH_2\cdot CH_2\end{smallmatrix}{>}CHPr^{\beta}$, produced; this compound, a highly refractive oil having the odour of camphor, is isomeric with that substance, and boils at 217—219°. The *oxime* separates from light petroleum in beautiful, lustrous crystals belonging to the monoclinic system. M. O. F.

Effect of Light on the Displacement of Bromine and Iodine from Organic Bromides and Iodides. By J. H. KASTLE and W. A. BEATTY (*Amer. Chem. J.*, 1897, **19**, 139—149).—By the action of light on the dibromo-derivative of benzenesulphonamide, bromine is liberated even in the presence of water. From the dichloro-derivative of parabromobenzenesulphonamide, chlorine is first liberated, which then displaces bromine from the benzene ring.

From the results of numerous experiments with bromo- and iodo-compounds, the authors draw the following conclusions.

Bromine and iodine are displaced from their most stable organic compounds by means of chlorine water, and it seems probable that in presence of sunlight, chlorine "not only displaces but replaces bromine and iodine in their aromatic derivatives." A. W. C.

Oxide of Dichlorodimethoxyquinoldibenzoate. By C. LORING JACKSON and H. A. TORREY (*Ber.*, 1897, **30**, 527—531. Compare Abstr., 1896, i, 155).—The oxide, $C_6Cl_2(OMe)_2(OBz)_2O$, is now shown to have the constitution

$$O{<}\begin{matrix}C(OBz)\cdot CCl\!:\!C\cdot OMe\\ \vert \qquad\qquad\quad \vert\\ C\!:\!CCl\text{———}C(OMe)\cdot OBz\end{matrix} \quad \text{or} \quad O{<}\begin{matrix}CCl{\ll}\begin{matrix}C\text{———}C(OMe)(OBz)\\ C(OBz)(OMe)\cdot C(OMe)\end{matrix}{\gg}CCl,\end{matrix}$$

that is, the oxygen atom is united with two carbons, which are either in the ortho- or meta-position relatively to one another.

Amylamine reacts with the oxide, yielding a purple-red compound, $C_5H_{11}\cdot NH\cdot C_6Cl_2O_2\cdot NH_2(OH)\cdot C_5H_{11}$, which melts at 181—182°. The *silver* and *barium* salts and the free phenol, *dichloroamylaminohydroxyquinone*, $C_5H_{11}\cdot NH\cdot C_6Cl_2O_2\cdot OH$, which melts at 186—187°, are described.

Sodium methoxide converts the oxide into the sodium salt of dichlorodimethoxyquinonedimethylhemiacetal. J. J. S.

Synthesis of Hydrogenised Derivatives of Resorcinol. By DANIEL VORLÄNDER (*Annalen*, 1897, **294**, 253—269).—The author discusses and summarises the results described in the following abstracts. M. O. F.

Synthesis and Hydrolysis of Dihydroresorcinol. By DANIEL VORLÄNDER (*Annalen*, 1897, **294**, 269—273. Compare Abstr., 1896, i, 20).—*Ethylic γ-acetylbutyrate* is a colourless liquid which boils at 221—222°; as already stated (*loc. cit.*), sodium ethoxide converts the salt into the sodium derivative of dihydroresorcinol. M. O. F.

Alkyldihydroresorcylic Acids. By DANIEL VORLÄNDER (*Annalen*, 1897, **294**, 273—301).—*Phenyldihydroresorcylic acid*, $OH\cdot C{<}\begin{smallmatrix}CH_2\cdot CHPh\\CH\text{———}CO\end{smallmatrix}{>}CH\cdot COOH$, is produced in the form of its methylic

salt when methylic malonate acts on benzylideneacetone in methylic alcohol solution under the influence of sodium methoxide; it melts at about 100°, liberating carbonic anhydride, and giving rise to phenyldihydroresorcinol. The *methylic* salt crystallises from boiling water or very dilute methylic alcohol in needles, and melts at 162°; the ethylic salt has been already described (Abstr., 1894, i, 527). Owing to the presence of a free hydroxylic group, these derivatives are phenolic in character, and consequently give rise to ethers. The *methyl* ether of the methylic salt crystallises from dilute methylic alcohol in lustrous plates, and melts at 110—111°; the *ethyl* ether of the ethylic salt boils and partly decomposes at 250—260° under a pressure of 30 mm.

Ethylic anilidophenyldihydroresorcylate,

$$NHPh\cdot C\begin{matrix}\diagup CH_2\cdot CHPh \diagdown \\ \diagdown CH \text{———} CO \diagup\end{matrix}CH\cdot COOEt,$$

is obtained by heating ethylic phenyldihydroresorcylate with 4 parts of aniline during 8—10 hours, and crystallises from alcohol in large prisms melting at 144—145°; resembling the other alkylamides, this substance is neutral in character, resists the action of hydroxylamine and alcoholic ammonia, and develops a brown coloration with ferric chloride. The *paratoluidido*-compound crystallises in colourless needles and melts at 214°; the *ethyl* derivative melts at 70°. When the ethyltoluidido-compound is heated with 10 parts of fuming hydrochloric acid in sealed tubes at 100° during 4 hours, ethyltoluidine is eliminated; the other alkylamides exhibit analogous behaviour under the influence of hydrochloric acid. The *paraphenetidido*-compound separates from alcohol in concentric groups of crystals, and melts at 168°.

Anilidophenyldihydroresorcylic acid,

$$NHPh\cdot C\begin{matrix}\diagup CH_2\cdot CHPh \diagdown \\ \diagdown CH \text{———} CO \diagup\end{matrix}CH\cdot COOH,$$

obtained by hydrolysing the ethylic salt with cold alcoholic potash, is a white powder which melts and evolves carbonic anhydride at about 190°, yielding *anilidophenyldihydroresorcinol*, which melts at 240°. *Toluidophenyldihydroresorcylic acid* yields *toluidophenyldihydroresorcinol* which melts at 215°; this substance is also produced when the attempt is made to crystallise the acid from hot glacial acetic acid.

The *semicarbazone* of ethylic phenyldihydroresorcylate,

$$NH_2\cdot CO\cdot NH\cdot N\colon C\begin{matrix}\diagup CH_2\cdot CHPh \diagdown \\ \diagdown CH_2 \text{———} CO \diagup\end{matrix}CH\cdot COOEt,$$

crystallises from alcohol in leaflets, and melts and decomposes at 208°. The phenylhydrazone melts at 130°, as stated by Knoevenagel, and not at 74—75°, as stated by Michael and Freer.

When ethylic phenyldihydroresorcylate is heated with benzaldehyde and acetic anhydride in sealed tubes at 150—160° during 8—10 hours, the *benzylidene* derivative, $CO\begin{matrix}\diagup CH_2\text{—}CHPh \diagdown \\ \diagdown C(CHPh)\cdot CO \diagup\end{matrix}CH\cdot COOEt$, is formed as a white substance which melts at 98°; the *diazobenzene* derivative, $CO\begin{matrix}\diagup CH_2\text{———}CHPh \diagdown \\ \diagdown C(N\cdot NHPh)\cdot CO \diagup\end{matrix}CH\cdot COOEt$, crystallises from alcohol, and melts at about 163°, previously becoming brown and undergoing decomposition.

Phenyldihydroresorcylonitrile, $OH\cdot C\begin{smallmatrix}\diagup CH_2\cdot CHPh\diagdown \\ \diagdown CH\text{——}CO\diagup\end{smallmatrix}CH\cdot CN$, is obtained in the form of sodium derivative when benzylideneacetone is heated with ethylic cyanacetate and alcoholic sodium ethoxide, and melts at about 180°; when treated with boiling, dilute sulphuric acid, phenyldihydroresorcinol is formed. The *methyl* ether crystallises in leaflets and melts at 173°. The *dimethyl* derivative of the nitrile, $OMe\cdot C\begin{smallmatrix}\diagup CH_2\cdot CHPh\diagdown \\ \diagdown CH\text{——}CO\diagup\end{smallmatrix}CMe\cdot CN$, is obtained by the action of methylic alcohol and sodium methoxide on the foregoing methyl ether and melts at 136°; the *methyl-nitrile*, $OH\cdot C\begin{smallmatrix}\diagup CH_2\cdot CHPh\diagdown \\ \diagdown CH\text{——}CO\diagup\end{smallmatrix}CMe\cdot CN$, is produced on hydrolysing the dimethylnitrile with aqueous sodium carbonate, and melts at 174°. The *hydroxylamine* derivative of the methyl-nitrile, $C_{14}H_{17}O_3N_3$, melts and evolves gas at 155°.

Anilidophenyldihydroresorcylonitrile,

$$NHPh\cdot C\begin{smallmatrix}\diagup CH_2\cdot CHPh\diagdown \\ \diagdown CH\text{——}CO\diagup\end{smallmatrix}CH\cdot CN,$$

crystallises from alcohol and melts at 230°; the *dioxime*,

$$NOH:C\begin{smallmatrix}\diagup CH_2\text{——}CHPh\diagdown \\ \diagdown CH_2\cdot C(NOH)\diagup\end{smallmatrix}CH\cdot CN,$$

crystallises from alcohol in colourless plates, and melts and decomposes at 182°. The *diazobenzene* derivative, $CO\begin{smallmatrix}\diagup CH_2\text{——}CHPh\diagdown \\ \diagdown C(N\cdot NHPh)\cdot CO\diagup\end{smallmatrix}CH\cdot CN$, is obtained as a yellow, crystalline precipitate on adding diazobenzene chloride to the nitrile dissolved in sodium carbonate; it melts at 110°, and becomes brownish-red after lapse of time.

Ethylic phenyldihydroresorcyloxalate,

$$CO\begin{smallmatrix}\diagup CH_2\cdot CHPh\diagdown \\ \diagdown CH_2\text{——}CO\diagup\end{smallmatrix}CH\cdot CO\cdot COOEt,$$

is obtained from benzylideneacetone and the sodium derivative of ethylic oxalacetate; it crystallises from alcohol in leaflets, and melts at 131°.

Ethylic orthochlorophenyldihydroresorcylate,

$$CO\begin{smallmatrix}\diagup CH_2\cdot CH(C_6H_4Cl)\diagdown \\ \diagdown CH_2\text{————}CO\diagup\end{smallmatrix}CH\cdot COOEt,$$

is prepared from the sodium derivative of ethylic malonate and orthochlorobenzylideneacetone; it melts at 142°. *Orthochlorobenzylideneacetone* is obtained from orthochlorobenzaldehyde and acetone in presence of 10 per cent. caustic soda, and boils at 189° under a pressure of 30 mm.; the *oxime* crystallises from dilute alcohol in lustrous, white needles, and melts at 117°.

Ethylic paranitrophenyldihydroresorcylate, which is formed when paranitrobenzylideneacetone is heated with alcoholic sodium ethoxide and ethylic malonate on the water bath, crystallises from alcohol in small, colourless prisms containing 1 molecule of the solvent; this is removed at 110°, and it then melts at 140°. *Ethylic metanitrophenyldihydroresorcylate* separates from alcohol in small, white crystals, and melts at 163°. *Metanitrobenzylideneacetone* crystallises from glacial acetic acid in small prisms, and melts at 94—95°; the phenylhydrazone melts at 155°.

Ethylic anisyldihydroresorcylate,

$$\mathrm{CO}\!<\!\begin{matrix}\mathrm{CH_2.CH(C_6H_4\cdot OMe)}\\ \mathrm{CH_2}\text{———————}\mathrm{CO}\end{matrix}\!>\!\mathrm{CH\cdot COOEt},$$

is obtained from anisylideneacetone and ethylic sodiomalonate, and also from ethylic paramethoxycinnamate and ethylic sodioacetoacetate; it crystallises from glacial acetic acid and melts at 160°. The *paraphenetidido*-derivative melts at 217°. *Ethylic paramethoxycinnamate* melts at 48—49°, and boils at 245° under a pressure of 120 mm.

Methylic phenyldimethyldihydroresorcylate,

$$\mathrm{CO}\!<\!\begin{matrix}\mathrm{CHMe\cdot CHPh}\\ \mathrm{CHMe}\text{——}\mathrm{CO}\end{matrix}\!>\!\mathrm{CH\cdot COOEt},$$

prepared from methylic sodiomalonate and benzylidenediethyl ketone, crystallises from methylic alcohol in small prisms melting at 185°; *phenyldimethyldihydroresorcylic acid* melts at about 100°, evolving carbonic anhydride, and yielding phenyldimethyldihydroresorcinol.

Ethylic styryldihydroresorcylate,

$$\mathrm{CO}\!<\!\begin{matrix}\mathrm{CH_2\cdot CH(CH\colon CHPh)}\\ \mathrm{CH_2}\text{———————}\mathrm{CO}\end{matrix}\!>\!\mathrm{CH\cdot COOEt},$$

crystallises from dilute alcohol in leaflets, and melts at 138°.

Ethylic furfuryldihydroresorcylate,

$$\mathrm{CO}\!<\!\begin{matrix}\mathrm{CH_2\cdot CH(C_4OH_3)}\\ \mathrm{CH}\text{—————}\mathrm{CO}\end{matrix}\!>\!\mathrm{CH\cdot COOEt},$$

crystallises from acetic acid and melts at 102°.

Methylic dimethyldihydroresorcylate, $\mathrm{CO}\!<\!\begin{matrix}\mathrm{CH_2\cdot CMe_2}\\ \mathrm{CH_2}\text{—}\mathrm{CO}\end{matrix}\!>\!\mathrm{CH\cdot COOMe}$, prepared from methylic malonate and mesitylic oxide, crystallises in long, slender needles melting at 102°; the aqueous solution develops a violet-brown coloration with ferric chloride. The *ethylic* salt melts at 75°, and forms a *sodium* derivative. The *paratoluidido*-derivative of the methylic salt melts at 147°. The *semicarbazone* of the ethylic salt crystallises in white scales and melts at 212°. M. O. F.

Alkyldihydroresorcinols. By DANIEL VORLÄNDER and JOH. ERIG (*Annalen*, 1897, **294**, 302—316).—Phenyldihydroresorcinol, obtained by crystallising phenyldihydroresorcylic acid from acetic acid, has been already described; the *sodium* derivative is crystalline, and the *lead* derivative a white precipitate. The *benzyl* ether crystallises from alcohol in small, lustrous leaflets, and melts at 129—130°. The ethyl ether and anilide have been already described by Stollé; the *ethylanilido-*, *paratoluidido-*, and *paraphenetidido*-derivatives melt at 135°, 215°, and 207° respectively. The *monoxime*, $\mathrm{CO}\!<\!\begin{matrix}\mathrm{CH_2\text{—}CHPh}\\ \mathrm{CH_2\cdot C(NOH)}\end{matrix}\!>\!\mathrm{CH_2}$, melts at 79°—82°, and the *dioxime* at 177°. The *diazobenzene* derivative, $\mathrm{CO}\!<\!\begin{matrix}\mathrm{CH_2}\text{——}\mathrm{CHPh}\\ \mathrm{C(N\cdot NHPh)\cdot CO}\end{matrix}\!>\!\mathrm{CH_2}$, crystallises from alcohol in beautiful, yellow leaflets, and melts at 172°; it forms a *dioxime* which crystallises from benzene and melts and decomposes at 228°. The *benzylidene* derivative, $\mathrm{CO}\!<\!\begin{matrix}\mathrm{CH_2\text{—}CHPh}\\ \mathrm{C(CHPh)\cdot CO}\end{matrix}\!>\!\mathrm{CH_2}$, crystallises from glacial acetic acid in beautiful prisms and melts at 232°.

Anisyldihydrorescinol, $\mathrm{CO}\!<\!\begin{matrix}\mathrm{CH_2\cdot CH(C_6H_4\cdot OMe)}\\ \mathrm{CH_2}\text{———————}\mathrm{CO}\end{matrix}\!>\!\mathrm{CH_2}$, crystallises

from alcohol in slender needles, and melts at about 185°; the *paraphenetidido*-derivative crystallises in small, white leaflets, melting at 226°, and the *dioxime* melts at 182—184°.

Phenyldimethyldihydroresorcinol, $CO<\begin{matrix}CHMe\cdot CHPh\\CHMe——CO\end{matrix}>CH_2$, melts at about 175°, and yields a yellow oil of disagreeable odour after some time.

Styryldihydroresorcinol, $CO<\begin{matrix}CH_2\cdot CH(CH:CHPh)\\CH_2————CO\end{matrix}>CH_2$, crystallises from alcohol or dilute acetic acid in white needles and melts at about 188°, when it decomposes.

Furfuryldihydroresorcinol, $CO<\begin{matrix}CH_2\cdot CH(C_4OH_3)\\CH_2———CO\end{matrix}>CH_2$, crystallises from hot water in prisms, and melts and decomposes at about 150°; the *anilido*-derivative crystallises from alcohol in small prisms and melts at 214°, the *dioxime* sinters at 175° and melts at about 180°, and the *diazobenzene* derivative at 152°.

Dimethyldihydroresorcinol, $CO<\begin{matrix}CH_2\cdot CMe_2\\CH_2—CO\end{matrix}>CH_2$, crystallises from hot water in plates, and melts at about 150°; the *paratoluidido*-derivative melts at 200°, and the *dioxime* at 176°. *Methylenebisdimethyldihydroresorcinol* crystallises from alcohol in needles, and melts at 189°.

M. O. F.

Constitution of Bromophenacetin. By O. Hodurek (*Ber.*, 1897, 30, 477—480).—*Acetobromophenetidine* (*bromophenacetin*),

$OEt\cdot C_6H_3Br\cdot NHAc, [OEt : Br : NHAc = 1 : 2 : 4]$,

obtained by the action of sodium hypobromite and hydrochloric acid on acetophenetidine dissolved in acetic acid, melts at 107°. When heated with concentrated hydrochloric acid, it is converted into *orthobromoparaphenetidine hydrochloride*, $OEt\cdot C_6H_3Br\cdot NH_2,HCl$, which is insoluble in hydrochloric acid; the free *base* melts at 46°, boils at 189° (pressure = 20 mm.), and has powerful reducing properties. The *sulphate* is a white, crystalline salt, readily soluble in water; the *mercurochloride* is only sparingly soluble. When the base is diazotised in alcoholic solution, it is converted into orthobromophenetoil, and this, on being heated with hydrochloric acid at 180—190°, yields orthobromophenol. The constitution of the original bromophenacetin is thus proved. *Diacetorthobromoparaphenetidide* is obtained when bromophenacetin is heated with acetic anhydride; it is a white, amorphous powder which melts at 90°.

When heated with hydriodic acid, bromophenacetin yields *orthobromoparamidophenol hydriodide*, which crystallises in yellow plates and has a powerful reducing action. The *hydrochloride* is extremely unstable.

A. H.

Phenacyl Compounds. By Franz Kunckell (*Ber.*, 1897, 30, 573—577. Compare Bischler, Abstr., 1892, 1465).—*Phenacylmetabromaniline*, $COPh\cdot CH_2\cdot NH\cdot C_6H_4Br$, is produced on mixing bromacetophenone with metabromaniline (2 mols.), and melts at 137°; the *hydrochloride* forms nacreous leaflets, and melts at 163°. *Phenacylparachloraniline* crystallises from a mixture of chloroform and alcohol, and melts at 167°. *Metanitrophenacylparachloraniline* crystallises in yellow

needles, and melts at 197°; it is isomeric with the *nitrophenacylparachloraniline* obtained by nitrating phenacylparachloraniline, which crystallises in reddish-yellow needles, and melts at 181°.

Phenacyl-as-*metaxylidine*, $COPh\cdot CH_2\cdot NH\cdot C_6H_3Me_2$, forms yellow needles, and melts at 98°; the *hydrochloride* is colourless, and melts at 147°. *Metanitrophenacyl*-as-*metaxylidine* crystallises from alcohol in dark-red needles and melts at 153°.

Phenacyl-α-naphthylamine and *phenacyl-β-naphthylamine* melt at 125° and 150° respectively. *Metanitrophenacyl-β-naphthylamine* crystallises in golden-yellow leaflets, and melts at 179°.

1-*Phenacyltetrahydroquinoline*, $COPh\cdot CH_2\cdot NC_9H_{10}$, crystallises from alcohol in yellow needles and melts at 104°; 1-*metanitrophenacyltetrahydroquinoline* forms golden-yellow leaflets and melts at 145°.

Phenacylparaphenetidine, $COPh\cdot CH_2\cdot NH\cdot C_6H_4\cdot OEt$, crystallises from alcohol in long, yellow needles and melts at 102°.

Benzoylmethyl paracresyl ether, $COPh\cdot CH_2\cdot O\cdot C_6H_4Me$, obtained by heating paracresol with bromacetophenone and alcoholic potash (compare Abstr., 1896, i, 151), melts at 68°. *Benzoylmethyl metatolyl ether* crystallises from alcohol in long needles and melts at 84°.

M. O. F.

Reduction of Picramide: Unsymmetrical Tetramidobenzene. By RUDOLF NIETZKI and HANS HAGENBACH (*Ber.*, 1897, 30, 539—545).—Although repeated attempts have been made to reduce picramide to the corresponding unsymmetrical tetramidobenzene, none have hitherto met with success, owing mainly to the inefficiency of the reducing agent. It is now found, however, that if finely powdered picramide is gradually added to a mixture of stannous chloride, tin, and hydrochloric acid, the yellow colour of the amide rapidly disappears, and colourless needles of the tri-acid hydrochloride of as-*tetramidobenzene*, $C_6H_2(NH_2)_4,3HCl + H_2O$, make their appearance. On dissolving this hydrochloride in water and adding alcohol, a *di-acid* hydrochloride free from water can be obtained, whilst on decomposing a solution of this with sulphuric acid and adding alcohol, a di-acid sulphate separates in hexagonal leaflets. Tetramidobenzene combines with diketones, forming primary quinoxalines, which still contain two free amido-groups; thus with benzil, 1:3-*diamido*-2′:3′-*diphenylquinoxaline*, $C_6H_2(NH_2)_2{<}{\begin{matrix}N:CPh\\ |\\ N:CPh\end{matrix}}$, is obtained in yellow leaflets melting at 260°; whilst with diacetyl, 1:3-*diamido*-2′:3′-*dimethylquinoxaline*, $C_6H_2(NH_2)_2{<}{\begin{matrix}N:CMe\\ |\\ N:CMe\end{matrix}}$, a pale yellow substance melting at 228° is produced. The latter forms a hydrochloride which crystallises in dark red needles.

With sodium acetate and acetic anhydride, tetramidobenzene yields a *tetracetyl* derivative, crystallising from water or from glacial acetic acid in colourless needles melting at 245°. On heating this with dilute sulphuric acid, three acetyl residues are eliminated, an *acetanhydro*-base of the constitution $C_6H_2(NH_2)_2{<}{\begin{matrix}N\\ NH\end{matrix}}{>}CMe$, being formed.

On oxidation with ferric chloride, tetramidobenzene is converted

into the hydrochloride of a *diamidoquinoneimide*, which, since it is identical with the oxidation product derived from ordinary triamidophenol, must have the constitution $[O:(NH_2)_2:NH = 1:2:6:4]$.

On partially reducing picramide with dilute ammonium sulphide, Norton and Elliott's *dinitrodiamidobenzene*, $[(NO_2)_2:(NH_2)_2 = 1:5:2:3]$, melting at 215°, is produced. The ortho-position of the amido-groups in this compound follows from the ready formation of an *acetanhydro*-compound, $C_6H_2(NO_2)_2<\genfrac{}{}{0pt}{}{N}{NH}>CMe$, and an *azimide*,

$$C_6H_2(NO_2)_2<\genfrac{}{}{0pt}{}{NH}{N}>N;$$

the former, which is produced on hydrolysing the acetyl derivative of the base with dilute sulphuric acid, crystallises in yellow needles melting at 242°, whilst the latter, formed by the action of nitrous acid on the hydrochloride, is obtained in colourless needles melting at 198°.

A *nitrotriamidobenzene* crystallising from alcohol in red scales which decompose at 260° without melting is produced when picramide is reduced with concentrated ammonium sulphide; it yields a *triacetyl* derivative melting at 243°, and a red, crystalline *acetanhydro*-base, $NH_2\cdot C_6H_2(NO_2)<\genfrac{}{}{0pt}{}{N}{NH}>CMe_2$, with diacetyl, the nitrotriamidobenzene yields a feebly basic quinoxaline, and on acetylation with glacial acetic acid and a little acetic anhydride, a monacetyl derivative; this, on treatment with nitrous acid, yields an azimide by means of which the constitution of the compound can be deduced, since on hydrolysing the acetyl derivative, the *nitramidoazimide*, $NO_2\cdot C_6H_2(NH_2)<\genfrac{}{}{0pt}{}{N}{NH}>N$, a dark yellow, infusible compound is produced, which on elimination of the amido-group by the ordinary method, yields a nitroazimide melting at 209°, and identical with the compound obtained by Hofmann from dinitraniline, and without doubt having the formula

$$NO_2\cdot C_6H_3<\genfrac{}{}{0pt}{}{N}{NH}>N \quad [N:NH:NO_2 = 2:3:5].$$

The position of the groups in the nitrotriamidobenzene must, therefore, be $[(NH_2)_3:NO_2 = 1:2:3:5]$. J. F. T.

Behaviour of Isomeric Diazotates towards Benzoic Chloride. By ARTHUR R. HANTZSCH (*Ber.*, 1897, **30**, 621—626).—The author finds, contrary to Bamberger's statement (this vol., i, 217), that both iso- and normal diazobenzenepotassium yield the same amount of nitrosobenzanilide when treated with benzoic chloride, and this takes place when a large excess of alkali and of benzoic chloride are present, and also when the theoretical amount of the chloride is used and only a slight excess of alkali, the normal and iso-compounds yielding the same amount of nitroso-compound. The parabromodiazotates behave in a similar manner. A. H.

Dynamical Researches on the Formation of Azo-dyes. By HEINRICH GOLDSCHMIDT and AUGUST MERZ (*Ber.*, 1897, **30**, 670—687).—The authors have quantitatively followed the formation of methyl-orange when an aqueous solution of dimethylaniline hydrochloride is

added to an aqueous solution of paradiazobenzenesulphonic acid. They accomplished this by estimating the amount of unaltered diazobenzenesulphonic acid remaining in solution at the end of given intervals of time, which was effected by boiling with water, and measuring the amount of nitrogen liberated. The conclusions arrived at are: 1. In the combination of the hydrochloride of a primary amine with diazobenzenesulphonic acid, it is the base, liberated from the hydrochloride by hydrolysis, which acts with the sulphonic acid as such. 2. An excess of hydrochloric acid retards the formation of the dye. 3. The concentration of the hydrochloride and of the sulphonic acid has no influence on the reaction. Experiments have also been made in order to determine the velocity of formation of methyl-orange from diazobenzenesulphonic acid and dimethylaniline in acetic acid solution. In this case, the dye is formed much more quickly than with hydrochloric acid, and the amount of acetic acid present has but little influence on the velocity of formation.

The reaction between metacresol and paradiazobenzenesulphonic acid, both in alkaline solution, has also been studied quantitatively. The results arrived at are: 1. In the formation of hydroxyazo-dyes from phenols and diazo-salts in alkaline solution, the active agents are the free phenol liberated by the hydrolytic action of the water on the alkali salt and the *syn*-diazo-compound. 2. An excess of alkali retards the formation of the dye. 3. The time required for the reaction to take place varies directly with the concentration. Experiments with other phenols are being carried out. J. J. S.

β-Orthonitrobenzylhydroxylamine. By CARL KJELLIN and K. G. KUYLENSTJERNA (*Ber.*, 1897, **30**, 517—518. Compare Paal and Poller, this vol., i, 184).—*β-Orthonitrobenzylisobenzaldoxime*,

$$O<\begin{matrix}CHPh\\ |\\ N\cdot CH_2\cdot C_6H_4\cdot NO_2\end{matrix},$$

obtained in the usual way by nitrobenzylating *syn*-benzaldoxime, crystallises in colourless needles and melts at 104—105°. It is readily soluble in alcohol and benzene, but only sparingly in light petroleum. When boiled for 10 minutes with sufficient hydrochloric acid (20 per cent.) to dissolve it when hot, it is readily decomposed into *β-orthonitrobenzylhydroxylamine*, $NO_2\cdot C_6H_4\cdot CH_2\cdot NH\cdot OH$, the *hydrochloride* of which separates on cooling. The latter crystallises in colourless needles, melts at 185°, and decomposes at 190°; it is only sparingly soluble in cold hydrochloric acid, readily, however, in alcohol and water; it also readily reduces Fehling's solution. The *free base* crystallises in silky needles, melts at 70°, and at 140° turns dark blue; when kept for some time, the base turns brown.

Phenylorthonitrobenzylhydroxycarbamide,

$$NO_2\cdot C_6H_4\cdot CH_2\cdot N(OH)\cdot CO\cdot NHPh$$

(m. p. 141°), is readily formed by the action of phenylcarbimide on a benzene solution of the base. J. J. S.

Constitution of Benzanilide. By N. KNIGHT (*Amer. Chem. J.*, 1897, **19**, 152—155).—By the action of benzoic chloride on benzenesulphonanilide or of benzenesulphonic chloride on benzanilide, dibenzoylanilide melting at 151° is produced. In both experiments, a beau-

tiful, white, crystalline substance melting at 231° was obtained, which proved to be the aniline salt of benzenesulphonic acid.

Other bye-products are formed, but in quantities insufficient for satisfactory examination. The most definite of these is a substance crystallising in plates and melting at 212°. A. W. C.

Action of Acid Chlorides on the Imido-ethers and Isoanilides: Structure of the Silver Salts of the Anilides. By HENRY L. WHEELER and PERCY T. WALDEN (*Amer. Chem. J.*, 1897, **19**, 129—139).—Substituted imido-ethers or isoanilides react with acid chlorides, as in the following example, $CH_3\cdot O\cdot CH\!:\!NPh + Ph\cdot COCl = CH_3\cdot O\cdot CHCl\cdot NPh\cdot COPh$. This additive product then looses the elements of methylic chloride, yielding a mixed diacid anilide,

$$O\!:\!CH\cdot NPh\cdot COPh.$$

These mixed diacid anilides are decomposed by alkalis, giving a monacid anilide of the higher acid group. The explanation of the ease with which this reaction takes place is the existence of a double linking between the carbon and nitrogen. That this action is not a double decomposition or replacement of the alkyl group by the acid radicle, is shown by the fact that non-substituted imido-ethers react with acid chlorides with elimination of hydrogen chloride instead of alkyl chloride.

The action of acid chlorides on the silver salts of the anilides is analogous to the above, addition first taking place with subsequent removal of silver chloride, proving that in these silver salts the silver is joined to oxygen.

Non-substituted imido-ethers react with acid chlorides as stated above, the eliminated hydrogen chloride combining with excess of the imido-ether; when the product of the action is treated with acid or exposed to air, it takes up a molecule of water, and then decomposes into a diacid amide, showing that the latter, like the diacid anilides, have both acid groups attached to a nitrogen atom. This decomposition is also analogous to the action of acids on the silver salts of amides or anilides.

Halogens react with imido-ethers, one molecule of the former with two of the latter, giving halogen imido-ethers and the halogen hydride salt of the imido-ether.

Formoacetanilide, $COH\cdot NAcPh$, is obtained by the action of acetic chloride on phenylformimidoethyl ether. It crystallises from a mixture of ether and light petroleum in beautiful, brittle crystals melting at 56—57°. Sodium hydroxide converts it into acetanilide.

Formobenzanilide, $COH\cdot NBzPh$, produced from benzoic chloride and phenylformimidoethyl ether, is a solid crystallising in needles and melting at 112°. By the action of sodium hydroxide, it is converted into benzanilide.

Formobenzenesulphonanilide, $COH\cdot NPh\cdot SO_2Ph$, obtained from the imido-ether and benzenesulphonic chloride, crystallises in colourless, radiating needles melting at 148—149°; on boiling it with sodium hydroxide, benzenesulphonanilide is produced.

Formobenzorthotoluidide and *formobenzoparatoluidide*,

$$COH\cdot NBz\cdot C_6H_4Me,$$

are produced when benzoic chloride acts on ortho- or para-tolylform-

imidoethyl ether respectively. The former melts at 91°, the latter at 102°. On treatment with alkali, the corresponding benzotoluides are obtained.

Benzoylbenzimidoethylic ether, $OEt\cdot CPh\!:\!NBz$, formed when benzoic chloride acts on benzimidoethyl ether, melts at 65°. Alkalis are without action on this substance; but acids readily convert it into dibenzamide.

Acetobenzimidomethylic ether, $OMe\cdot CPh\!:\!NAc$, the product of the action of acetic chloride on benzimidomethyl ether, is a liquid boiling at 139° under a pressure of 15 mm. Dilute sulphuric acid converts it into acetobenzamide, which melts at 120°. The corresponding *acetobenzimidoethylic ether* is a liquid which distils at 151° under a pressure of 17 mm.

Benzobromimidomethylic ether and *benzoiodo-imidomethylic ether* are oily compounds obtained by the direct action of the halogen on benzimidomethyl ether. A. W. C.

Isoimides. By P. Hojonides van der Meulen (*Rec. Trav. Chim.*, 1896, 15, 282—287. Compare Hoogewerff and van Dorp, Abstr., 1896, i, 314).—*α-Hemipinobenzylamic acid*,

$$COOH\cdot C_6H_2(OMe)_2\cdot CO\cdot NH\cdot C_7H_7,\ [=1:3:4:2],$$

which is readily formed on gently warming hemipinic anhydride with an aqueous solution of benzylamine, is conveniently purified by precipitating it from its solution in hydrochloric acid and recrystallising the product from alcohol. It melts at 171—172°, is insoluble in ether, sparingly soluble in water, but readily so in acetone and chloroform. When the alcoholic mother liquor from the α-acid is diluted with water, it yields a small amount of the isomeric β-acid. α-Hemipinobenzylamic acid, when treated with acetic chloride, yields *α-hemipinobenzylisoimide*, $O{<}{\overset{CO}{\underset{C(:NC_7H_7)}{}}}{>}C_6H_2(OMe)_2$, the mixture is heated at 60° for 7 minutes and poured into carbon bisulphide, when the *hydrochloride* of the isoimide separates as an oil which quickly solidifies; it is collected, added to dry ether, and decomposed with a slight excess of aqueous potash (30 per cent.), care being taken to keep the mixture cold. The isoimide is obtained from its ethereal solution in fine needles which melt at 99—100°. It is necessary to expedite the above reactions, as the compound is readily decomposed by water, yielding hemipinobenzylamic acid.

Hempinobenzylimide, $C_7H_7\cdot N{<}{\overset{CO}{\underset{CO}{}}}{>}C_6H_2(OMe)_2$, is readily obtained by heating α-hemipinobenzylamic acid until the water which is produced just disappears. It crystallises in needles, melts at 128—132°, is readily soluble in chloroform and acetone, sparingly in water, and insoluble in ether.

β-Hemipinobenzylamic acid, $COOH\cdot C_6H_2(OMe)_2\cdot CO\cdot NH\cdot C_7H_7$ [= 2 : 3 : 4 : 1] is obtained when hemipinobenzylimide is warmed with caustic soda (5 per cent.) on the water bath. It melts at 161—162° and as regards its solubility resembles the α-acid. The *β-isoimide* crystallises in glistening plates and melts at 80—82°.

Phthalophenylisoimide $C_6H_4{<}{\overset{CO}{\underset{C(:NPh)}{}}}{>}O$, crystallises in small

needles, melts at 115—117°, and is slowly transformed into the imide when heated at 250°. J. J. S.

Halogenised Ketones. By FRANZ KUNCKELL (*Ber.*, 1897, 30, 577—579).—*Paratolyl bromomethyl ketone*, $CH_2Br\cdot CO\cdot C_6H_4Me$, is obtained by adding bromine to a solution of the original ketone in glacial acetic acid, and after an interval of 12 hours, heating the liquid on the water bath; it crystallises from alcohol in colourless leaflets, and melts at 48—50°.

Paratolyl chloromethyl ketone, $CH_2Cl\cdot CO\cdot C_6H_4Me$, is prepared by the action of chloracetic chloride on toluene in presence of aluminium chloride; it crystallises in long needles and melts at 67°. *Metaxylyl chloromethyl ketone* and *paraxylyl chloromethyl ketone* melt at 62—63° and 32° respectively. *Pentethylphenyl chloromethyl ketone*,

$$CH_2Cl\cdot CO\cdot C_6Et_5,$$

forms short, white needles and melts at 104°. M. O. F.

Formation of Benzoic and Propionic Peroxides by Active Oxygen. By W. P. JORISSEN (*Zeit. physikal. Chem.*, 1897, 22, 54—59).—The author has previously shown that, during the slow oxidation of benzaldehyde by oxygen, an equal portion of the gas is rendered 'active.' If acetic anhydride is mixed with the benzaldehyde and the surface increased by the addition of sand, the volume of oxygen absorbed is double that necessary for oxidation to benzoic acid. A similar result was obtained when the sand was omitted, in both cases benzoic peroxide was obtained from the residue, but in the absence of acetic anhydride, benzoic acid alone was produced. The author considers the results are to be expressed by the equations:

$$C_6H_5\cdot COH + O_2 = C_6H_5\cdot COOH + O\text{ (active)}$$
$$(CH_3\cdot CO)_2 + O\text{(active)} = (CH_3\cdot CO)_2O_2$$
$$(CH_3\cdot CO)_2O_2 + 2C_6H_5\cdot COH + O_2 = (C_6H_5\cdot CO)_2O_2 + 2CH_3\cdot COOH.$$

Similar experiments with propaldehyde and acetic anhydride gave similar results, but the ratio of oxygen absorbed to that absorbed in the absence of the anhydride was 1·75 : 1. The author explains this departure from the previous value of 2 : 1 to the fact that the vapour pressure of the aldehyde is much greater than that of the anhydride, and hence that the "active" oxygen does not find sufficient anhydride in its vicinity, when formed. L. M. J.

Pseudophenylacetic Acid. By EDUARD BUCHNER (*Ber.*, 1897, 30, 632—636. Compare Abstr., 1896, i, 230).—*Isophenylacetic acid*, $C_7H_7\cdot COOH$, is the name applied by the author to the unsaturated acid obtained on hydrolysing ψ-phenylacetamide with aqueous soda; it crystallises from much boiling water in flat needles and melts at 71°. Although the substance decolorises a cold solution of potassium permanganate immediately, it is quite distinct from pseudophenylacetic acid, because it undergoes no change when exposed to air, and develops a yellow coloration when dissolved in concentrated sulphuric acid. A solution of ethylic ψ-phenylacetate in concentrated sulphuric acid is initially cherry-red, rapidly becoming violet, and finally blue, exhibiting moderately strong fluorescence; the absorption spectrum is very characteristic, and it is noteworthy that dihydrobenzene, when dissolved in alcoholic sulphuric acid, develops an intense blue coloration (Von

Baeyer, Abstr., 1892, 1075). The *barium* and *calcium* salts of isophenylacetic acid are readily soluble, but crystallise from highly concentrated solutions; the *silver* salt is very sensitive to light, and yields a crystalline distillate when heated. The *amide* crystallises from much boiling ether in flat, yellowish needles, and melts at 129°; hydrolysis with aqueous soda regenerates the acid. Isophenylacetic acid *monohydrobromide*, $C_7H_8Br\cdot COOH$, is obtained from the acid and glacial acetic acid saturated with hydrogen bromide at 0° (4 parts); it crystallises from a mixture of ether and petroleum, melts and evolves gas at 127°, and the solution in excess of sodium carbonate immediately decolorises potassium permanganate. The *dihydrobromide*, $C_7H_9Br_2\cdot COOH$, prepared by using 8 parts of the saturated solution of hydrogen bromide, crystallises from ether and melts at 164°, evolving a small quantity of gas; boiling water decomposes the substance, which undergoes no change in air, and alkaline potassium permanganate is at once reduced. When the dihydrobromide is reduced with sodium amalgam, an unsaturated, oily *tetrahydroisophenylacetic acid* is produced, further reduction giving rise to a mixture of substances; one of these is a saturated *acid*, $C_6H_{10}O_2$, which crystallises in needles, melts at 124—126°, and is volatile in an atmosphere of steam. The main product of ultimate reduction, however, is *hexahydroisophenylacetic acid*, a saturated oil, having an intensely disagreeable odour; the *amide* melts indefinitely at 184—186°. M. O. F.

Paranitrophenoxyacetic and Paramidophenoxyacetic Acids, and some of their Derivatives. By C. Kym (*J. pr. Chem.*, 1897, [ii], **55**, 113—123).—Paranitrophenoxyacetic acid is most conveniently prepared by hydrolysis of the ethylic salt, which is itself produced almost quantitatively when ethylic chloracetate is heated at 180° with sodium nitrophenol. The ethylic salt crystallises in pale yellow, lustrous needles, and melts at 75—76°. *Paranitrophenoxyacetanilide*, $NO_2\cdot C_6H_4\cdot O\cdot CH_2\cdot CO\cdot NHPh$, crystallises in pale, yellow, lustrous needles melting at 170—171°. *Paramidophenoxyacetanilide*, prepared by reducing the nitro-derivative with tin and hydrochloric acid, crystallises in long, colourless needles melting at 104—105°; *paracetamidophenoxyacetanilide* crystallises in lustrous, white plates, melting at 204—205°. *Paramidophenoxyacetic acid*, $NH_2\cdot C_6H_4\cdot O\cdot CH_2\cdot COOH$, which Fritsche (Abstr., 1880, 319) was unable to obtain, can be prepared by reducing the nitro-acid with tin and hydrochloric acid; it crystallises with $1H_2O$ in compact, white needles or prisms, and does not melt below 312°. The *ammonium* salt crystallises in slender needles, melting at 201—202°; the *hydrochloride* is a white, crystalline mass, which is soluble in alcohol. The *benzoyl*-derivative crystallises in fascicular groups of needles melting at 194—195°; and the *acetyl*-derivative in long, lustrous needles melting at 175—176°. It possesses antipyretic properties, but not to the same extent as phenacetin, which it resembles in constitution. Orthonitrophenol behaves towards ethylic chloracetate in a similar manner to the para-compound. The derivatives thus obtained have already been described. A. H.

Paramidophenoxyacetic Acid. By Curtis C. Howard (*Ber.*, 1897, **30**, 545—548).—*Paramidophenoxyacetic acid*, $NH_2\cdot C_6H_4\cdot O\cdot CH_2\cdot COOH$,

can be prepared either by the reduction of Fritzsche's paranitroparaphenoxyacetic acid, by means of tin and acetic acid, and hydrolysing the acetyl compound thus produced, or by the action of the sodium salt of paracetamidophenol on sodium monochloracetate. It separates from boiling water, in which it is only sparingly soluble, in prismatic crystals containing $1H_2O$; this it looses at 100°, and then does not melt at 300°. The *acetyl* derivative crystallises in slender needles with $1H_2O$, which it loses at 100°, and melts when anhydrous at 174°.

Uramidophenoxyacetic acid, $NH_2\cdot CO\cdot NH_2\cdot C_6H_4\cdot O\cdot CH_2\cdot COOH$, prepared from the amido-acid in the usual way, has a slightly acid taste; it crystallises from hot water in flat prisms melting at 195°, and containing $2H_2O$. The *ethylic* salt forms white, anhydrous needles melting at 148°.

The *hydrazine* of *paraphenoxyacetic acid*,

$$NH_2\cdot NH\cdot C_6H_4\cdot O\cdot CH_2\cdot COOH,$$

prepared by V. Meyer and Lecco's method, separates from its aqueous solution, on the addition of alcohol, in small, white crystals containing $1H_2O$, melts at 146°, and becomes yellow on exposure to the air.

J. F. T.

Tautomerism of Orthoaldehydic Acids, III. By CARL T. LIEBERMANN (*Ber.*, 1897, **30**, 691—697. Compare Abstr., 1896, i, 232 and 682).—In the present communication, it is shown that methylnoropianic acid reacts with aromatic bases in exactly the same way as opianic acid, the compounds produced having the oxyphthalide structure; they are, however, soluble in soda, since they contain phenolic hydroxyl groups.

ψ-Ethylic methylnoropianate, $\begin{matrix} O\text{—}CH\cdot OEt \\ | \qquad | \\ CO\cdot C_6H_2(OMe)\cdot OH \end{matrix}$, is obtained by boiling methylnoropianic acid for half an hour with ethylic alcohol; on adding light petroleum to its benzene solution, it separates in colourless needles melting at 104—106°. It is readily soluble in dilute soda, yielding the sodium derivative, which, however, is only sparingly soluble in concentrated soda solution; the acid is readily recovered from this pseudo-salt by boiling it with water.

ψ-Methylic methylnoropianate melts at 67—71°.

n-Ethylic methylnoropianate, $OMe\cdot C_6H_2(OH)(CHO)\cdot COOEt$, is formed when silver methylnoropianate is boiled for several hours with ethylic iodide; it melts at 102—103°, is sparingly soluble in benzene and in hot water, and differs from the ψ-ethylic salt in not being hydrolysed by boiling water.

An aqueous solution of mucobromic acid (1 mol.), on treatment with aniline ($\frac{3}{4}$ mol.), yields the anilide of mucobromic acid, but with excess of aniline (2 mols.), Hill and Palmer's mucohydroxybromic acid anilide, $OH\cdot C_4HBr(NPh)\cdot COOH$, is formed (Abstr., 1888, 451). Graebe and Bossel's benzaldehydedicarboxylic acid (*Annalen*, **290**, 215) reacts with α-naphthylamine to form an *α-naphthylamide*, $C_{10}H_8\cdot N{:}CH\cdot C_6H_3(COOH)_2$ melting at 202—207°. That the naphthylamide has the above constitution, and not that of an oxyphthalide, was proved by the analyses of its *barium* and *silver* derivatives.

The author recommends the formation of this α-naphthylamide as a

ready means of purifying Graebe and Bossel's acid, the melting point of which is given as 162—165°, and not 175—178°. J. J. S.

δ-Ketonic Acids. By DANIEL VORLÄNDER and ARTHUR KNÖTZSCH (*Annalen*, 1897, **294**, 317—336).—*Ethylic a-acetylglutarate* is obtained by the action of ethylic acetoacetate on ethylic acrylate under the influence of sodium ethoxide, and boils at 174—177° under a pressure of 30 mm.; hydrolysis with cold alcoholic potash gives rise to glutaric acid, whilst boiling hydrochloric acid resolves the substance into carbonic anhydride and γ-acetylbutyric acid. The *oxime* of γ-acetylbutyric acid crystallises from water or benzene, and melts at 103—104°; the *lactone*, $CH_2<\begin{matrix}CH_2\cdot CO\\ CH:CMe\end{matrix}>O$, is a colourless liquid which boils at 194—195°, and the *amide* and *paratoluidide* melt at 114° and 123° respectively.

Acetonylbenzylmalonic acid, $COMe\cdot CH_2\cdot CHPh\cdot CH(COOH)_2$, is produced on treating ethylic phenyldihydroresorcylate with a boiling solution of barium hydroxide during 6—8 hours; it is an amorphous substance, which dissolves very readily in water, and melts at 115°, evolving carbonic anhydride. Stollé obtained the same substance by hydrolysing ethylic phenyldihydroresorcinoldicarboxylate.

γ-Acetyl-β-phenylbutyric acid, $CH_2Ac\cdot CHPh\cdot CH_2\cdot COOH$, is obtained by hydrolysing phenyldihydroresorcinol and ethylic phenyldihydroresorcylate (compare Abstr., 1894, i, 528); the *ethylic* salt boils at 186—189° under a pressure of 20 mm., and is converted into phenyldihydroresorcinol under the influence of sodium ethoxide free from alcohol suspended in absolute ether. The *oxime* crystallises from water in lustrous plates, and melts at 127°, and the *lactone*, $CHPh<\begin{matrix}CH_2\cdot CO\\ CH:CMe\end{matrix}>O$, has a peculiar odour, and boils at 177—180° under a pressure of 33 mm. The *amide* crystallises from water in small prisms containing $1H_2O$, and melts at about 128° when rapidly heated; the *amide anhydride* is obtained on heating the amide during several hours at 90—100°, and crystallises from water in long needles melting at 137°. The latter substance is also produced when ethylic acetylphenylbutyrate is heated in sealed tubes with alcoholic ammonia; nitrous acid converts the amide anhydride, $C_{12}H_{13}ON$, into the *compound* $C_{12}H_{14}O_3N_2$, which crystallises in small, white needles, melts and decomposes at about 188°, and does not give Liebermann's reaction. The *methylamide* of acetylphenylbutyric acid is obtained from the anhydride and methylamine and melts at 143°; the *methylamine* compound of the methylamide, $2C_{13}H_{17}O_2N + NH_2Me + H_2O$, crystallises in long needles, and yields the methylamide at 100°. The *anilide* crystallises from alcohol or acetic acid in leaflets, and melts at 135°.

The lactone of δ-hydroxy-β-phenylcaproic acid boils at 271—273° under a pressure of 17 mm. according to Michael and Freer, whilst Stollé states that the substance boils at 194—195° under a pressure of 13 mm.; the authors have prepared it by reducing γ-acetyl-β-phenylbutyric acid with sodium amalgam, and find that it boils at 190—192° under a pressure of 20 mm.

γ-Acetyl-β-anisylbutyric acid, $CH_2Ac\cdot CH(C_6H_4\cdot OMe)\cdot CH_2\cdot COOH$, is obtained by hydrolysing ethylic anisyldihydroresorcylate with barium

hydroxide, and after crystallisation from water melts at 104°; the *oxime* melts at 169°.

γ-Benzoyl-β-phenylbutyric acid, $CH_2Bz \cdot CHPh \cdot CH_2 \cdot COOH$, is obtained by hydrolysing the crude salt produced from ethylic sodiomalonate and benzylideneacetophenone, and fusing the intermediate dibasic *acid*, $CH_2Bz \cdot CHPh \cdot CH(COOH)_2$, which melts and loses carbonic anhydride at 144°; the ketonic acid crystallises from glacial acetic acid in prisms and melts at 155—156°. The *oxime* melts at 144—146°, and a *lactone*, $CHPh{<}\begin{smallmatrix}CH_2 \cdot CO\\ CH{:}CPh\end{smallmatrix}{>}O$ crystallises from ether in needles.

[With KARL HOBOHM.]—*Isobutyrylanisylbutyric acid*,

$$CHMe_2 \cdot CO \cdot CH_2 \cdot CH(C_6H_4 \cdot OMe) \cdot CH_2 \cdot COOH,$$

is obtained by fusing the acid, which arises from the action of ethylic sodiomalonate on anisylidenemethyl isopropyl ketone; it crystallises from acetic acid or boiling water, and melts at 118°. The *amide* crystallises from boiling water in slender, white needles, and melts at 158—159°. *Anisylidenemethyl isopropyl ketone*,

$$OMe \cdot C_6H_4 \cdot CH{:}CH \cdot CO \cdot CHMe_2,$$

is prepared from methyl isopropyl ketone and anisaldehyde under the influence of 10 per cent. caustic soda; it melts at 28° and boils at 217—219° under a pressure of 40 mm. M. O. F.

Molecular Rearrangement of Phenylsulphonamic Acid. By EUGEN BAMBERGER and E. HINDERMANN (*Ber.*, 1897, **30**, 654—655).—Having shown that sulphurous anhydride converts phenylhydroxylamine into a mixture of phenylsuphonamic and orthamidobenzenesulphonic acids, an attempt was made to convert the former into the latter; by heating barium phenylsulphonamate at 180° during $4\frac{1}{2}$ hours, it is converted, however, into the barium salt of paramidobenzenesulphonic acid. M. O. F.

Constitution of "Patent Blue." BY ERNST ERDMANN and HUGO ERDMANN (*Annalen*, 1897, **294**, 376—392. Compare Fritsch, this vol., i, 72).—Basing their conclusion on a synthesis which determines the position of at least one sulphonic group in the colouring matter, the authors ascribe to patent-blue, which they investigated in the form of its magnesium salt, the constitutional formula

$$[C_6H_4{<}\begin{smallmatrix}NEt_2 \text{———} SO_3\\ C\,(C_6H_4 \cdot NEt_2)\end{smallmatrix}{>}C_6H_2(OH) \cdot SO_3]_2Mg + 3H_2O.$$

The salt is exceptionally hygroscopic, and may be preserved many weeks in the exsiccator without becoming constant in weight; at 110°, however, upwards of 5 per cent. of moisture is removed, the remaining three molecules resisting a temperature of 160—170°, at which gradual decomposition occurs. Although the substance contains two sulphonic groups, it is not a hydrogen magnesium salt, because the composition remains unaltered after treatment with a boiling solution of barium hydroxide and subsequent saturation with carbonic anhydride.

Metahydroxytetrethylparadiamidotriphenylcarbinol,

$$OH \cdot C_6H_4 \cdot C(C_6H_4 \cdot NEt_2)_2 \cdot OH,$$

is obtained by heating patent-blue with concentrated hydrochloric acid during 66 hours in a reflux apparatus; it separates as a greenish precipitate on treatment with alkali as a dark green, amorphous powder,

which forms a solution of the same colour in alcohol and in very dilute hydrochloric acid, the solution in excess of hydrochloric acid being yellow. The substance is indifferent towards hot caustic soda.

When patent-blue is treated with a boiling 5 per cent. solution of caustic soda, nitrogen is eliminated quantitatively as diethylamine, the liquid becoming violet, and finally red, owing to the production of a colouring matter of the rosolic acid series.

A colouring matter identical with the technical form of patent blue has been already synthesised by the authors (D. R. P., No. 46384) from metanitrobenzaldehyde and diethylaniline. The aldehyde and the base are heated with dehydrated oxalic acid during many hours on the water bath; the condensation product, metanitroleuco-brilliant-green is reduced with stannous chloride and hydrochloric acid, the amido-compound diazotised, and converted into hydroxyleuco-brilliant-green. The latter is treated with fuming sulphuric acid at ordinary temperatures, and finally oxidised with lead peroxide and sulphuric acid; the magnesium salt of the colouring matter obtained in this way exhibits all the properties of the technical form.

Whilst this process throws no light on the positions occupied by the sulphonic groups, a synthesis has been effected which shows that the free sulphonic radicle is in the para-position with regard to the carbon atom combined with the substituted aniline complexes. Nitration converts parachlorobenzaldehyde into parachlorometanitrobenzaldehyde, which yields sodium metanitrobenzaldehydeparasulphonate under the influence of sodium sulphite; reduction, diazotisation, and conversion into metahydroxybenzaldehydeparasulphonic acid then follow, the last-named condensing with diethylaniline to form metahydroxyleuco-brilliant-green-parasulphonic acid. When this substance is added to 5 parts of fuming sulphuric acid containing 20 per cent. of anhydride, a second sulphonic group is introduced, and the product yields patent-blue on oxidation with lead peroxide and sulphuric acid.

The *leuco-base of parachlorometanitro-malachite-green*,

$$NO_2\cdot C_6H_3Cl\cdot CH(C_6H_4\cdot NMe_2)_2,$$

is obtained by heating parachlorometanitrobenzaldehyde with dimethylaniline and zinc chloride on the water bath, and crystallises from alcohol in golden-yellow needles melting at 133—134°; it is oxidised by sulphuric acid and lead peroxide to a green colouring matter. The *leuco-base of parachlorometamido-malachite-green* crystallises from alcohol in white needles and melts at 167—167·5°.

Metanitroleuco-malachite-green-parasulphonic acid,

$$NO_2\cdot C_6H_3(HSO_3)\cdot CH(C_6H_4\cdot NMe_2)_2,$$

is obtained by the action of potassium sulphite on parachlorometanitroleuco-malachite-green, and also by condensing metanitrobenzaldehydeparasulphonic acid with dimethylaniline; the *sodium* salt crystallises in yellowish leaflets.

Metamidoleuco-brilliant-green-parasulphonic acid is obtained by heating potassium metanitrobenzaldehydeparasulphonate (2 parts) with diethylaniline (6 parts), zinc chloride (2 parts), and concentrated sulphuric acid (1 part), at first in the water bath, and finally at 110° during 14 hours; the product is rendered alkaline, freed from diethylaniline by a current of steam, and reduced with hydrochloric acid and zinc

dust. On saturating the filtered liquid with ammonia, the *ammonium* salt of the sulphonic acid separates out; the *sodium* salt is crystalline.

Metahydroxyleuco-brilliant-green-parasulphonic acid,

$$OH\cdot C_6H_3(HSO_3)\cdot CH(C_6H_4\cdot NEt_2)_2,$$

is produced on diazotising the foregoing amido-compound, and eliminating nitrogen under the influence of heat; it is also obtained by heating sodium hydroxybenzaldehydesulphonate with dehydrated oxalic acid and diethylaniline at 110°. The substance is colourless, but rapidly becomes green when exposed to air; the *sodium* salt crystallises in leaflets. As already stated, when the sulphonic acid is added to fuming sulphuric acid, and the product oxidised with lead peroxide and sulphuric acid, patent-blue is formed.

The authors discuss the constitution of the colouring matter, and criticise the observations of Fritsch (*loc. cit.*). M. O. F.

Action of Nitrogen Oxides on Mercurydiphenyl and on Nitrosobenzene. By EUGEN BAMBERGER (*Ber.*, 1897, **30**, 506—513).—The action of nitric oxide on mercurydiphenyl and similar substances was studied in the hope of synthesising nitroso-derivatives of aromatic hydroxylamines. Nitric oxide, however, in the absence of all traces of air, does not react with mercurydiphenyl, but in the presence of air small quantities of mercuryphenyl nitrate, $HgPh\cdot NO_3$, and of diazobenzene nitrate are formed.

Nitrous anhydride in chloroform solution readily reacts with mercurydiphenyl, even at low temperatures, yielding mercuryphenyl nitrate, diazobenzene nitrate, and nitrosobenzene. Nitric peroxide also readily reacts on mercurydiphenyl, the two products being mercuryphenyl nitrate and nitrosobenzene. As nitrosobenzene readily combines with nitric oxide, it follows that the nitrous anhydride reacts, at any rate to some extent, as a mixture of nitric oxide and peroxide. A second product was also obtained by the action of nitric oxide on nitrosobenzene. It is a yellow substance; the amount, however, was small, and it could not be obtained in a pure state.

Orthonitrosotoluene and parabromonitrosobenzene also react with nitric oxide, yielding orthodiazotoluene nitrate and parabromodiazobenzene nitrate respectively. It appears to be a characteristic property of all true nitroso-compounds to react with nitric oxide. Other aromatic derivatives of mercury appear to behave in much the same way as mercurydiphenyl.

The author suggests nitrosobenzene as a reagent for testing for nitric oxide or nitrous anhydride in nitric peroxide. J. J. S.

Zinc Dust in the Presence of Acetic Acid as an Oxidising Agent. By OSSIAN ASCHAN (*Ber.*, 1897, **30**, 657—658).—Sudborough (Trans., 1897, **219**) has shown that benzoin, when treated with zinc dust and acetic acid, yields benzil, an oxidation product of benzoin, together with deoxybenzoin. The author has observed a similar case of oxidation in the case of camphororthoquinone (Claisen and Manasse, Abstr., 1894, i, 479). A solution of the quinone (5 grams), in glacial acetic acid (30 grams) becomes quite hot on the addition of zinc dust, and the yellowish colour gradually disappears. When evaporated to half its bulk, and then treated with water, the solution yields camphoric

anhydride, formed from the camphorquinone by oxidation. No appreciable quantity of any other substance could be isolated. J. J. S.

Action of Nitrosodimethylaniline on certain Bromo-derivatives of Gallic Acid. By ALEXANDRE BIÉTRIX (*Bull. Soc. Chim.*, 1896, [iii.], **15**, 404—408).—By the action of nitrosodimethylaniline hydrochloride on dibromogallic acid, a blue substance is obtained, which appears to be *bromogallocyanin*, $C_{14}H_{11}NO_3ClBr\cdot COOH$.

Similarly, methylic dibromogallate gives, with nitrosodimethylaniline, the *methylic* salt of bromogallocyanin. In solution in water or alcohol, this has a violet colour, which turns red on the addition of an acid.

The anilide of dibromogallic acid gives, with nitrosodimethylaniline, the *anilide* of bromogallocyanin; it is a violet substance, soluble in alcohol, but only slightly so in water and benzene. M. W. T.

Action of Alphylhydrazines on β-Naphthaquinone. By EUGEN BAMBERGER (*Ber.*, 1897, **30**, 513—516).—According to Zincke and Bindewald (Abstr., 1885, 391), the same product is obtained from α-naphthol and diazobenzene as from α-naphthaquinone and phenylhydrazine, whereas β-naphthol or β-naphthaquinone, when treated with the same reagents, yields two isomeric substances, which probably may be represented by the two formulæ $\underset{\beta}{O:}C_{10}H_6\underset{\alpha}{:}N_2HPh$ for the compound obtained from β-naphthol and diazobenzene, and $\underset{\alpha}{O:}C_{10}H_6\underset{\beta}{:}N_2HPh$, that from β-naphthaquinone and phenylhydrazine. The author now shows this view to be correct, since β-naphthaquinone and paranitrophenylhydrazine in acetic acid solution yield the same dye (m. p. 235—236°) which the author had previously prepared from α-naphthol and paranitrodiazobenzene, namely $O:C_{10}H_6:N_2H\cdot C_6H_4\cdot NO_2$ (compare Abstr., 1895, i, 351).

Similarly, β-naphthaquinone with paranitrophenylhydrazine and with orthonitrorthotolylhydrazine, yields the same dyes as have been previously obtained from α-naphthol (*loc. cit.*).

Paranitrorthotolylhydrazine was prepared by Bamberger and Kraus' method (Abstr., 1896, i, 610). On the addition of potassium sulphite to the solution of diazotised paranitrorthotoluidine, it yields a crystalline mass of *potassium paranitrorthotolylhydrazinesulphonate*,

$$NO_2\cdot C_6H_3Me\cdot N(SO_3K)\cdot NH\cdot SO_3K$$

[Me : NO_2 : N = 2 : 4 : 1]. This is then warmed on the water bath with concentrated hydrochloric acid, the precipitated crystals collected, dissolved in water, and the paranitrorthotolylhydrazine precipitated by the addition of sodium acetate. It crystallises from boiling alcohol or xylene in golden or orange-yellow needles, and melts at 179—180°.

J. J. S.

Camphor Leaf Oil. By DAVID HOOPER (*Pharm. J. Trans.*, 1896, [iv.], **2**, 21—22).—The leaves of camphor trees from two different localities were distilled with water for 6 hours. The sample from Otacamund gave about 1 per cent. of essential oil, which was slightly yellow, had a sp. gr. = 0·9322 at 15°, and gave a rotation of + 9·4° in a 200 mm. tube; camphor was only present to the extent of about 10 or 15 per cent. Leaves from Naduvatam gave about 0·5 per cent. of

oil containing 75 per cent. of camphor dissolved and suspended in it. The strained oil had a sp. gr. $=0.9314$ at 15°, and gave a rotation of + 54° in a 200 mm. tube. R. R.

Hydroxycamphor. By OTTO MANASSE (*Ber.*, 1897, **30**, 659—670). —A number of compounds described as hydroxycamphor have been prepared by different chemists (compare Wheeler, *Annalen*, **146**, 83; Schiff, Abstr., 1880, 892; Kachler and Spitzer, Abstr., 1880, 324; Schrötter, Abstr., 1882, 66, and Schmiedeberg, *Zeit. Physiol. Chem.*, **3**, 422). The author, by the reduction of camphororthoquinone, has prepared yet another hydroxycamphor which in many respects resembles the compound described by Schmiedeberg as campherol, but differs altogether in its physiological action.

When camphorquinone prepared from isonitrosocamphor by means of nitrous acid is treated with zinc dust and acetic or sulphuric acid, it yields a mixture of hydroxycamphor and camphoric anhydride (see Manasse, this vol., i, 288), but camphorquinone prepared by the bisulphite method yields simply hydroxycamphor; the author thinks, therefore, that the camphoric anhydride was originally present as an impurity in the quinone obtained by the action of nitrous acid on isonitrosocamphor. A quantitative yield of hydroxycamphor may be obtained by the following method. The quinone is dissolved in ordinary ether, hydrochloric or sulphuric acid is added, and then, in small quantities at a time, zinc dust made into a cream with water, the mixture being well shaken until it becomes colourless. The acid solution, separated from the ethereal layer, is saturated with common salt and again extracted with ether. On distilling off the ether from the combined ethereal solutions, a white, crystalline compound is obtained, which is most conveniently purified by distillation with steam, or by recrystallisation from a little light petroleum. Either aluminium amalgam, or zinc dust and acetic acid may be used as the reducing agents; in the latter case, the temperature must not exceed 30—40°, as otherwise an oily bye-product is formed.

Hydroxycamphor purified by distillation in steam is a snow-white, practically odourless powder. It melts at 203—205°, and is soluble in cold water to the extent of about 2 per cent.; it melts in hot water and is fairly readily soluble on boiling, separating again in a crystalline form as the solution cools. It can easily be "salted out" from its aqueous solutions, and is extremely soluble in all organic solvents with the exception of light petroleum. Although not so readily volatile as either camphor or camphorquinone, it is yet volatile to a slight extent with ether vapour. Its solutions are dextrorotary, the specific rotation being $+9.5°$. It does not form salts with alkalis, although it is sparingly soluble in caustic soda solution. On oxidation with an acetic acid solution of chromic anhydride, it is converted into camphorquinone; with hydrogen peroxide in alkaline solution, however, it yields camphoric acid. The latter process of oxidation takes place much more slowly than the similar oxidation of camphorquinone to camphoric acid. The physiological properties of the compound are given in detail; its chief action appears to be a slackening of the respiratory function.

Hydroxycamphorsemicarbazone, $C_8H_{14}<\begin{matrix}CH\cdot OH\\ |\\ C:N\cdot NH\cdot CO\cdot NH_2\end{matrix}$, crystallises in hard, glistening prisms and melts at 182—183°. The corresponding *anhydride* (?) $C_8H_{14}<\begin{matrix}CH-NH\\ |\\ C:N\cdot NH\end{matrix}>CO$, which is sometimes formed together with the semicarbazone, melts and decomposes at 208—209°.

Hydroxycamphorphenylhydrazone crystallises from dilute alcohol in yellowish needles, and melts at 137·5°.

Hydroxycamphoroxime (isonitrosoborneol), $C_8H_{14}<\begin{matrix}CH\cdot OH\\ |\\ C:NOH\end{matrix}$, crystallises from a mixture of ether and light petroleum, or from aqueous alcohol, in splendid, glistening pyramids. It melts at 86—87° and contains $\frac{1}{2}H_2O$; when anhydrous it melts at 121—122°.

Benzoyl and *acetyl* derivatives of hydroxycamphor could only be obtained in the form of syrups.

Hydroxycamphorphenylsulphone, $C_8H_{14}<\begin{matrix}CH\cdot O\cdot SO_2Ph\\ |\\ CO\end{matrix}$, crystallises in pyramids and melts at 95—96°. J. J. S.

High Boiling Point Constituents of Oil of Celery. By Giacomo L. Ciamician and Paul G. Silber (*Ber.*, 1897, **30**, 492—501).—A small portion of the high boiling point oil and residue obtained on distilling celery seed oil is soluble in alkali, and consists of palmitic acid together with substances of phenolic character, one of which crystallises in broad, white needles, melts at 66—67°, and has the formula $C_{16}H_{20}O_3$.

The remainder of the oil may be divided into two portions by boiling with 25 per cent. aqueous potash, the insoluble residue consisting of terpene-like compounds of the composition $C_{15}H_{24}$, whilst the solution is found to contain two acids. The first of these, *sedanolic acid*, $C_{12}H_{20}O_3$, very readily forms a lactone, and may thus be separated from the *sedanonic acid* which accompanies it.

Sedanolic acid can only be obtained pure by acidifying the alkali solution of the acid at a low temperature, dissolving the acid in ether, and precipitating it from this solution by adding light petroleum; it crystallises in white needles, is insoluble in water, and melts at 88—89°. A solution of the acid in sodium carbonate at once reduces potassium permanganate solution. The *silver* salt has the normal composition.

The lactone, *sedanolide*, $C_{12}H_{18}O_2$, prepared by distilling the acid, boils at 185° (under a pressure of 17 mm.). It is a thick, colourless oil, and is the odoriferous constituent of oil of celery, in which it appears to occur in the free state. Its constitution has not yet been definitely ascertained.

Sedanonic acid, $C_{12}H_{18}O_3$, is insoluble in water, and crystallises from benzene in compact, white crystals melting at 113°; the *silver* salt is soluble in hot water. It is a well-marked ketonic acid, the *phenylhydrazone* of which is extremely unstable, and melts at 130—131°; the *oxime*, $C_{12}H_{18}O_2$:NOH, is a stable substance which separates

from benzene in white crystals having a fatty lustre and melting at 128°. A. H.

Products of Decomposition of Sedanonic Acid. By GIACOMO L. CIAMICIAN and PAUL G. SILBER (*Ber.*, 1897, 30, 501—506. Compare the preceding abstract).—When sedanonoxime is warmed with concentrated sulphuric acid, it undergoes molecular change and is converted into Δ^2-*Tetrahydrophthalo-n-butylamic acid*,

$$COOH\cdot C_6H_8\cdot CO\cdot NH\cdot C_4H_9,$$

which crystallises in colourless prisms melting at 171°; this compound, when heated with dilute sulphuric acid, undergoes hydrolysis, yielding *n*-butylamine and Δ^2-tetrahydrophthalic acid (Baeyer, Abstr., 1890, 1275), which was recognised by its properties and by the fact that on reduction it was converted into the fumaroid form of hexahydrophthalic acid.

Sedanonic acid itself, therefore, probably has one of the two following formulæ.

$$\begin{array}{l} CH_2\cdot CH_2\cdot CH\cdot CO\cdot C_4H_9 \\ CH_2\cdot CH : C\cdot COOH \end{array} \qquad \begin{array}{l} CH_2\cdot CH : C\cdot CO\cdot C_4H_9 \\ CH_2\cdot CH_2\, CH\cdot COOH \end{array}.$$

A. H.

Luteolin. By JOSEF HERZIG (*Ber.*, 1897, 30, 656. Compare this vol., i, 94).—The bye-product obtained in preparing luteolin triethyl ether is colourless, and melts at 146—149°; it is probable that this substance is tetrethylluteolin. M. O. F.

Cochineal Dye. By CARL T. LIEBERMANN and HUGO VOSWINCKEL (*Ber.*, 1897, 30, 688—691).—The dye stuff obtained from 1 kilo. of cochineal or from 150 grams of cochineal-carmine was dissolved in 3 litres of acidified water, and to this solution 125 grams of potash dissolved in 250 c.c. of water was first added, and then 100 grams of potassium persulphate mixed with water, when the violet colour gradually changed to yellowish-brown. The liquid was then filtered from precipitated inorganic salts, the filtrate acidified, evaporated to one-sixth its volume, and extracted several times with ether containing a small quantity of alcohol; on distilling off the ether, a solid residue was obtained containing several organic acids. The yield is not good, but is much better when smaller quantities of the cochineal dye are operated on at a time. The aqueous solution of the residue, when boiled with animal charcoal and allowed to cool, deposited a small quantity of needle-shaped crystals of a sparingly soluble acid which the author terms coccinic acid. The amount of this is about one-tenth of the total ethereal residue.

Coccinic acid, $C_9H_8O_5$(?), is only sparingly soluble in water, but dissolves readily in alcohol. It melts and decomposes at 293°.

On treating the filtrate from the coccinic acid with lead acetate, it yields a precipitate consisting of the lead salt of a new acid, which is termed cochinelic acid.

Cochinelic acid, $C_{10}H_8O_7$(?), is moderately soluble in cold water, readily in hot, and extremely so in alcohol, glacial acetic acid or acetone; benzene, aromatic hydrocarbons, and ether, however, dissolve it but sparingly, whilst in light petroleum, chloroform or carbon bisulphide it is practically insoluble. It crystallises in small

needles and melts at 224—225°, carbonic anhydride being evolved at the same time. The *calcium* salt, which is readily soluble in water, apparently has the composition $C_{10}H_6O_6Ca$.

With ferric chloride, it gives a red coloration, indicating the presence of phenolic hydroxyl groups, and with bromine water it yields a *tribromocresotic acid*, $OH\cdot C_6Br_3Me\cdot COOH$, which melts at 220°.

J. J. S.

Synthesis of Ethereal Salts of Substituted Diketodihydropyrrolinecarboxylic Acids by means of Ethylic Oxalacetate and Aldehydoamido-Bases. By ROBERT SCHIFF and C. BERTINI (*Ber.*, 1897, **30**, 601—604).—When ethylic oxalacetate is heated with benzylideneaniline, or benzaldehyde and aniline, *ethylic* 1 : 2-*diphenyldiketodihydropyrroline-3-carboxylate*, $NPh<\begin{matrix}CHPh\cdot CH\cdot COOEt\\ CO\text{——}CO\end{matrix}$, is formed. It crystallises well and melts at 171°; with sodium ethoxide, it yields a *sodium* compound, $C_{19}H_{16}NaNO_4$. Two *isomeric monoximes* have been prepared; one of these is almost insoluble in ether and melts at 224°; the other is readily soluble and melts at 110°. Similar compounds have been obtained from a number of amido-compounds. Paratoluidine yields a *substance*, $C_6H_4Me\cdot N<\begin{matrix}CHPh\cdot CH\cdot COOEt\\ CO\text{——}CO\end{matrix}$, which melts at 152—153°.

The *compound* from metanitraniline, $NO_2\cdot C_6H_4\cdot C_4NH_2PhO_2\cdot COOEt$, melts at 199—200°, and $C_{10}H_7\cdot C_4NH_2PhO_2\cdot COOEt$, that from β-naphthylamine, at 142—143°. The *substance* obtained from amidoazobenzene, $N_2Ph\cdot C_6H_4\cdot C_4NH_2Ph\cdot COOEt$, forms crystals which are insoluble in alcohol, and melt at 215°, whilst that from metamidobenzoic acid, $COOH\cdot C_6H_4\cdot C_4NH_2PhO_2\cdot COOEt$, melts at 230°. Ethylic acetate, aniline, and metanitrobenzaldehyde yield a *substance*, $NPh<\begin{matrix}CH(C_6H_4\cdot NO_2)\cdot CH\cdot COOEt\\ CO\text{————}CO\end{matrix}$, which melts at 208—209°.

When ethylic acetoacetate is heated with a little alcohol and a molecular proportion of benzylideneaniline, an additive compound,

$$NHPh\cdot CHPh\cdot CHAc\cdot COOEt,$$

is formed which melts at 103—104°, and is readily decomposed by acids.

A. H.

Stereochemical Researches in the Piperidine Series. By CARL D. HARRIES (*Annalen*, 1897, **294**, 336—375. Compare Abstr., 1896, i, **317**).—By the investigation of 4-amido-2 : 2 : 6-trimethylpiperidine, obtained on reducing vinyldiacetonamidoxime (*loc. cit.*), an interesting case of stereochemical isomerism has been brought to light. The base in question, having the constitutional formula

$$NH<\begin{matrix}CHMe\cdot CH_2\\ CMe_2\text{—}CH_2\end{matrix}>\overset{*}{C}H\cdot NH_2,$$

should yield, on treatment with nitrous acid, the vinyldiacetonalkamine (m. p. 123°) obtained by E. Fischer on reducing vinyldiacetonamine; in preparing vinyldiacetonalkamine, however, in order to compare it with the product of the action of nitrous acid on the amidopiperidine derivative, it was found that on working with large quantities of sub-

stance at a higher temperature, an isomeric vinyldiacetonalkamine is produced melting at 160—161°. As this compound might also arise from the action of nitrous acid on an amidotrimethylpiperidine isomeric with the derivative already obtained on reducing vinyldiacetonamidoxime with zinc dust and alcoholic hydrochloric acid at temperatures below 10°, the oxime was reduced with sodium and boiling amylic alcohol; in this way, an isomeric 4-amido-2 : 2 : 6-trimethylpiperidine is produced which, on treatment with nitrous acid, yields the new vinyldiacetonalkamine melting at 160—161°.

The isomerism under discussion is doubtless due to the carbon atom indicated by an asterisk in the foregoing formula, and in this respect is analogous to that recognised by Willstätter (Abstr., 1896, i, 451) as existing between tropine and *ψ*-tropine, the latter of which is produced on treating the former with hot sodium amyloxide; on endeavouring to convert one vinyldiacetonalkamine into the other under the influence of the same agency, it was found that both forms (m. p. 120—121° and m. p. 160—161°) yield a third modification which melts at 137—138°. Careful investigation of these three substances has shown that the form which melts at 137—138° is the stable modification of the form melting at 160—161°, the third substance (m. p. 120—121°) being an intimate mixture of both isomerides; the author refers to them as the *α*- and *β*-modifications respectively, and represents them by the following expressions:

$$NH\left\langle\begin{array}{l}CHMe\cdot CH_2\searrow\\ \qquad\qquad OH\rightarrow CH\\ CMe_2{-}CH_2\nearrow\end{array}\right. \qquad\qquad NH\left\langle\begin{array}{l}CHMe\cdot CH_2\searrow\\ \qquad\qquad\qquad CH\cdot OH.\\ CMe_2{-}CH_2\nearrow\end{array}\right.$$

α-Vinyldiacetonalkamine (stable) m. p. 137—138°. *β*-Vinyldiacetonalkamine (labile) m. p. 160—161°.

Although the mixture which melts at 120—121° does not represent a third modification, it closely simulates an individual substance crystallising in beautiful, six-sided prisms which are quite distinct from the cubes melting at 137—138° and the long, lustrous prisms which melt at 160—161°; it is not possible, moreover, to resolve the mixture of bases by repeated crystallisation from benzene, an operation which does not raise the melting point above 120—121°, and the author is disposed to regard as probable the existence of some form of combination, more especially as 4-amido-2 : 2 : 6-trimethylpiperidine, which is certainly an individual substance, yields the characteristic crystals of the mixture when treated with nitrous acid.

The isomerism of the two amidotrimethylpiperidines is of the same character as that of the vinyldiacetonalkamines, the form already described (Abstr., 1896, i, 318) constituting the *α*-modification, whilst the base obtained on reducing the oxime with sodium and boiling amylic alcohol is the *β*-isomeride; the former of these yields, with carbon bisulphide, the *α*-thiocarbamate,

$$a,\ N\left\langle\begin{array}{l}CHMe\cdot CH_2\searrow\\ CS\cdot SH\ NH_2\rightarrow CH\\ CMe_2{-}CH_2\nearrow\end{array}\right. \qquad\qquad b,\ NH\left\langle\begin{array}{l}CHMe\cdot CH_2\searrow\\ SH\cdot CS\cdot NH\rightarrow CH,\\ CMe_2{-}CH_2\nearrow\end{array}\right.$$

which melts at 144—145°, and when treated with boiling water yields the *b*-thiocarbamate which melts at 187—188° (*loc. cit.*), whilst the *β*-modification yields a single thiocarbamate which melts at 197—198°.

Vinyldiacetonamidoxime *dihydrochloride* is obtained on adding ether to an alcoholic solution of the oxime which has been saturated with hydrogen chloride; it is very hygroscopic, and when heated at 100° yields the *monhydrochloride* which crystallises from absolute alcohol in leaflets.

The α-modification of 4-amido-2 : 2 : 6-trimethylpiperidine is obtained, as already stated (*loc. cit.*), by reducing vinyldiacetonamidoxime with zinc dust and alcoholic hydrogen chloride at temperatures below 5°; in order to separate it from the isomeride which is also produced, the mixed hydrochlorides are treated with absolute alcohol, in which the hydrochloride of the β-modification is insoluble. When the base is treated in ethereal solution with carbon bisulphide (1 mol.), the *a-thiocarbamate*, $C_9H_{18}N_2S_2$, is obtained as a hygroscopic substance which melts and decomposes at 144—145°; it is excessively soluble in water, and mercuric chloride gives with the solution a bright orange precipitate, which gradually becomes white when heated, and although mercuric sulphide is not precipitated under these circumstances, the compound at once separates when a hot solution of the mercuric salt is added to the hot aqueous thiocarbamate. This is due to the production of the *b*-thiocarbamate, which is formed when an aqueous solution of the α-modification is boiled, and crystallises in lustrous prisms melting at 187—188° (*loc. cit.*); mercuric chloride gives a reddish precipitate with the aqueous solution, becoming black when heated.

a-Amidotrimethylpiperidine eso-thiocarbamide, $N\left\langle\begin{array}{l}CHMe{\cdot}CH_2\\ CS\text{——}NH\\ CMe_2\text{—}CH_2\end{array}\right\rangle CH$, the substance obtained on treating the thiocarbamates with mercuric chloride, melts at 77—78° (compare *loc. cit.*); the *hydrochloride* melts and decomposes at 254—255°, and the *aurochloride* crystallises in yellow, oblique prisms which melt and decompose at 108—109°.

The *β-modification* of 4-amido-2 : 2 : 6-trimethylpiperidine is obtained by dissolving vinyldiacetonamidoxime in hot amylic alcohol and adding sodium in small pieces to the boiling solution; it is a colourless liquid which boils at 82—84° under a pressure of 22 mm. The *hydrate* crystallises in beautiful, transparent plates, melts at 20°, and boils at 91—92° under a pressure of 22 mm.; the *hydrochloride* and *hydrobromide* are crystalline, the *aurochloride* resembles that of the α-modification, the *platinochloride* forms fascicular groups of long needles, and the *picrate* crystallises in rhombic prisms. The *acetyl* derivative melts at 85—86°; the *acetate* of this base melts and decomposes at 130—132°, and the *aurochloride* crystallises in beautiful, concentric groups of leaflets. Carbon bisulphide converts β-amidotrimethylpiperidine into a *thiocarbamate*, $C_9H_{18}N_2S_2$, which crystallises in small, six-sided prisms and melts at 197—198°; when the aqueous solution is boiled, hydrogen sulphide is evolved, and β-amidotrimethylpiperidine is regenerated, along with a very small quantity of an oil which crystallises.

a-Vinyldiacetonalkamine, $NH\left\langle\begin{array}{l}CHMe{\cdot}CH_2\\ \qquad\quad OH\\ CMe_2\text{—}CH_2\end{array}\right\rangle CH$, is produced along with the β-modification when vinyldiacetonamine is reduced with sodium amalgam, and crystallises from benzene in regular cubes melting at

137—138° and boiling at 211°; the *hydrochloride* crystallises in prisms, and the *aurochloride* and *platinochloride* crystallise in large, yellow, rectangular plates.

β-Vinyldiacetonalkamine, $NH<\begin{matrix}CHMe\cdot CH_2\\CMe_2-CH_2\end{matrix}>CH\cdot OH$, crystallises from benzene in silky, lustrous prisms, melts at 160—161°, and boils at 204—205°; the *hydrochloride* is an oil, the *aurochloride* crystallises in beautiful, yellow plates, and the *platinochloride* in fascicular needles. Sodium amyloxide converts it into the α-modification. M. O. F.

Syntheses in the Piperidine Series. By Felix B. Ahrens (*Ber.*, 1897, **30**, 533—537).—The compound $C_{10}H_{20}N_2$, obtained by the electrolysis of nitrosopiperidine, and described in a previous paper as dipiperidyl, was evidently not quite pure, as on recrystallising it from acetone, large, transparent crystals melting at 96—97°, and corresponding in composition with *diperideine*, $C_{10}H_{18}N_2$, are obtained. The *monobenzoyl* derivative of this compound melts at 145—147°.

Reduction of diperideine with tin and hydrochloric acid gives rise to two isomeric compounds, separable by means of their platinochlorides; on adding platinic chloride to the acid reduction product after it has been freed from tin by hydrogen sulphide, an orange-yellow, crystalline precipitate is instantly formed, which, on recrystallisation from water, yields the pure *platinochloride*, $(C_5H_{11}N),H_2PtCl_6 + 2H_2O$, in microscopic needles melting at 253—254°. The corresponding *aurochloride* forms needles melting and decomposing at 195°, the *free* base obtained, on adding potassium hydroxide to a solution of the hydrochloride and extracting with ether, although yielding a solid carbonate when its ethereal solution is saturated with carbonic anhydride, has not as yet been obtained in a crystalline condition.

On concentrating the filtrate from the platinochloride first precipitated, red, flat crystals of an isomeric *platinochloride*, $(C_5H_{11}N),H_2PtCl_6 + 2H_2O$, separate; this melts at 220°, and at 230° effervesces vigorously. The corresponding *aurochloride* forms large needles melting and decomposing at 218°—219°. The *hydrochloride*, $C_5H_{11}N,HCl$, consists of needles stable at 280°; the *hydrobromide*, which also crystallises in needles, does not melt below 270°, the corresponding *base*, which, like its isomeride, forms a solid carbonate, is an oil becoming partially crystalline when kept for a long time.

The matter is still under investigation, the author proposing to further study the behaviour of homologues of nitrosopiperidine under the same conditions. J. F. T.

Tetrahydroquinoline-1-sulphonic Acid. By Adolph Claus and Wilhelm Günther (*J. pr. Chem.*, 1897, [ii], **55**, 94—112).—*Tetrahydroquinoline-1-sulphonic acid*, which is best prepared by reducing quinoline-1-sulphonic acid with tin and hydrochloric acid, forms fascicular groups of slender crystals and decomposes at 240—242°. It yields well crystallised salts, of which the *potassium, barium, calcium, copper*, and *silver* salts have been prepared. *Methylic tetrahydroquinoline-1-sulphonate methiodide* is obtained by heating the silver salt with methylic iodide, but very readily loses hydrogen iodide, and passes

into *methyltrihydroquinoline*-1-*sulphonic methylbetaine*, which crystallises in hard, vitreous prisms melting at 251°.

When tetrahydroquinolinesulphonic acid is fused with potash, the sole product is 1-hydroxyquinoline. The sulphonic group is best removed by distilling the ammonium salt with ammonium chloride in a current of ammonia. When heated with hydrochloric acid, quinoline is formed together with a base which contains sulphur, but has not yet been obtained pure.

When the sulphonic acid is treated with bromine in presence of water, derivatives of quinoline and quinolinesulphonic acid are always obtained, together with bromotetrahydroquinolinesulphonic acid; the chief products under such circumstances are 1-bromoquinoline; a compound melting at 101°, which is probably 1 : 3-*dibromoquinoline*; 1 : 3 : 3′-tribromoquinoline (in largest amount), and a *tetrabromoquinoline* which melts at 255°, and is also formed by the further bromination of 1 : 3 : 3′-tribromoquinoline. In addition to these, quinolinesulphonic acid itself and its *monobromo*-derivative, which crystallises in red needles and does not melt below 360°, are also formed. On the other hand, when the bromination is carried out in chloroform solution, 3-bromotetrahydroquinoline-1-sulphonic acid is formed almost quantitatively; this crystallises in slender, lustrous needles melting at 245°. The constitution of this acid has not been definitely settled, but since it yields 1 : 3 : 3′-tribromoquinoline on further bromination in aqueous solution, most probably it has the one assigned to it above. The *ammonium, potassium, silver, calcium, barium, cobalt, nickel*, and *lead* salts have all been prepared. When the silver salt is heated with methylic iodide, 3-*bromomethyltrihydroquinoline*-1-*sulphonic methylbetaine*, $C_9H_8BrNMe_2(SO_3)$ is produced; this crystallises in long, colourless needles and melts at 253°.

When the brominated acid is fused with potash, it yields 1-hydroxyquinoline.

The acid previously described as 4-bromoquinoline-2-sulphonic acid is in reality 3-bromoquinoline-1-sulphonic acid, since on reduction it yields tetrahydroquinoline-1-sulphonic acid. A. H.

Constitution of the Compounds of Antipyrin with Phenols. By Gustave Patein (*Compt. rend.*, 1897, **124**, 233—235).—Phenylmethylpyrazolone does not form combinations with β-naphthol, resorcinol, quinol, or salicylic acid in presence of alcohol. It follows that in the case of antipyrin it is the more electropositive nitrogen 2 that combines with the phenols, and the formation of the compounds cannot be reconciled with E. von Meyer's view that the constitution of antipyrin is of the same general character as that of the betaines.

C. H. B.

Dinitrilophenylhydrazones and the Products of their Intramolecular Change. By Reinhold Walther (*J. pr. Chem.*, 1897, [ii], **55**, 137—144).—When the phenylhydrazone of diacetonitrile,

$$CN \cdot CH_2 \cdot CMe{:}N \cdot NHPh,$$

melting at 97°, is heated with hydrochloric acid, it is converted into an isomeric substance which crystallises in compact prisms and melts at 116°. This isomeride appears to be 1-*phenyl*-3-*methyl*-5-*imidopyrazolone*,

$NPh<\begin{matrix} N = CMe \\ C(:NH)\cdot CH_2 \end{matrix}$. If the original hydrazone melting at 97° is treated in alcoholic solution with gaseous nitrous acid, it yields a *nitroso* derivative, $C_{10}H_{10}N_4O$, which crystallises in carmine red, lustrous prisms melting at 195—196°; this substance, when heated with alcoholic hydrochloric acid at 120°, is converted into Knorr's 1-phenyl-3-methyl-4-isonitroso-5-pyrazolone (*Annalen*, **238**, 185), and the same compound is obtained by the direct action of sodium nitrite and hydrochloric acid on the above-mentioned isomeride of the hydrazone (m. p. 116°).

The results obtained above show that the isomeride produced from the hydrazone of diacetonitrile has a constitution analogous to that proposed by Burns (Abstr., 1893, i, 314) for the corresponding isomeride of diacetonitrileoxime. A. H.

A Condensation Product of Formaldehyde with Antipyrine. By E. Marcourt (*Bull. Soc. Chim.*, 1896, [iii], **15**, 520).—When a solution containing equivalent quantities of antipyrine and formaldehyde is allowed to stand for a few days, a crystalline substance is deposited which appears to be a direct condensation product of the two substances. *Formopyrine* forms crystals which belong to the monoclinic system and melts at 142°. It is slightly soluble in hot water, insoluble in ether and benzene, and soluble in alcohol. In moist air, it appears to be stable at the ordinary temperature, but when heated to 110°, or if kept in a vacuum, the crystals decrepitate and lose formaldehyde. Formopyrine acts as a weak base, forming the salts $C_{12}H_{14}N_2O_2,HCl$, $(C_{12}H_{14}N_2O_2)_2,H_2SO_4$, $C_{12}H_{14}N_2O_2,H_2SO_4$, $C_{12}H_{14}N_2O_2,HNO_3$, $C_{12}H_{14}N_2O_2,H_3PO_4$, $C_{12}H_{14}N_2O_2,C_2H_2O_4$, which are white, crystalline substances.

The author considers that formopyrine has probably the constitution represented by the formula $\begin{matrix} CO\cdot NPh \\ CH\cdot CMe \end{matrix}>NMe<\begin{matrix} CH_2 \\ O \end{matrix}$ from analogy with a similar compound formed by the condensation of antipyrine with chloral. M. W. T.

Dimethylpyrazine. By Felix B. Ahrens and Georg Meissner (*Ber.*, 1897, **30**, 532—533).—Ten grams of isonitrosoacetone was dissolved in 200 grams of sulphuric acid (5 per cent.) and placed in a porous cell, which in its turn was surrounded by sulphuric acid of the same strength. Platinum foil was used as the anode, and lead foil as the cathode. The density of the cathode current was 3—7 ampères per 100 sq. cm., and the voltage 4—6. The complete electrolysis required 3—5 hours, the product was then extracted with ether, rendered alkaline, and distilled so long as the distillate was still strongly alkaline. The distillate was then acidified with hydrochloric acid and precipitated with mercuric chloride. The precipitate, when dissolved in water, treated with hydrogen sulphide, and then rendered alkaline, gave the free base, dimethylpyrazine or ketine, which was extracted with ether. J. J. S.

Pyrazines and Piperazines. VII. By Carl Stoehr (*J. pr. Chem.*, 1897, [ii], **55**, 49—77. Compare Abstr., 1893, i, 486).—The pyrazines

are converted by reduction directly into piperazines, no intermediate di- or tetra-hydropyrazines having been observed. The piperazines, which closely resemble the aliphatic diamines, are obtained in two modifications, which are probably stereoisomerides, one form being produced in small amount only. The rise of boiling point produced in the pyrazines by the introduction of a methyl group is 18°, whereas in the piperazine series it is only about 7°, hence, although the lower members of the piperazine series boil at higher temperatures than the corresponding pyrazines, the reverse is the case with the higher members. Of the two isomeric forms of the piperazines, the β-modification, that which is produced in smaller amount, usually has a slightly higher boiling point, does not crystallise so well, and yields a hydrochloride which is more readily soluble in alcohol than that of the α-form.

α-2 : 5-Dimethylpiperazine has previously been described; it crystallises in tabular forms of the monosymmetric system

$$[a : b : c = 1\cdot7026 : 1 : 2\cdot9809. \quad \beta = 86° \; 34'].$$

β-2 : 5-*Dimethylpiperazine* crystallises less readily than the α-compound and forms rhombic tablets; $a : b : c = 1\cdot6534 : 1 : 2\cdot7416$. It melts at 114—115°, 4° below the α-compound, and boils at the same temperature as the latter, namely, 162°. The *hydrochloride*, $C_6H_{14}N_2,2HCl + H_2O$, is much more readily soluble in water and alcohol than that of the α-compound; the *hydrobromide*, $C_6H_{14}N_2,2HBr + H_2O$ forms prismatic, rhombic crystals which lose their water at 110—120° and then melt at 287—288°; the *sulphate* forms lustrous tablets; the *dichromate* deflagrates at 140—141° and closely resembles the α-compound, forming tabular, asymmetric crystals. The *phosphate*, $C_6H_{14}N_2,2H_3PO_4 + H_2O$, crystallises in asymmetric prisms. The *tartrate*, $C_6H_{14}N_2,C_4H_6O_6 + 1\frac{1}{2}H_2O$, crystallises in needles or irregular prisms, the anhydrous salt melting at 222—223°. The *picrate* is almost insoluble in cold water. The *dibenzoyl* derivative melts at 147—148° (previously stated as 151—152°) and crystallises in monosymmetric prisms.

II. [With P. Brandes.]—α-*Trimethylpiperazine*, $\begin{array}{l} CHMe\cdot NH\cdot CHMe \\ | \qquad\qquad\quad | \\ CHMe\cdot NH\cdot CH_2 \end{array}$ boils at 169—169·5°, and when cooled with ice, solidifies in lustrous prisms; the *hydrochloride*, which crystallises in lustrous tablets and decomposes above 270° without melting, is only sparingly soluble in boiling alcohol; the *platinochloride* crystallises with $2H_2O$; the *picrate* decomposes at 278—279°. The *dibenzoyl* derivative forms anhydrous, rhombic tablets and melts at 190°. The *dinitrosamine*, $C_7H_{14}N_2(NO)_2$, crystallises in almost colourless plates, melting at 95—96°.

β-2 : 3 : 5-*Trimethylpiperazine* boils at 174—175° and could not be obtained in the solid form; the *hydrochloride* is readily soluble in alcohol and only crystallises with difficulty; the *platinochloride* crystallises with $2H_2O$ in four-sided prisms; the *picrate* melts and decomposes at 246°. The *dibenzoyl* derivative and the dinitrosamine could not be obtained in the solid form.

III. [With W. Detert; compare Abstr., 1893, i, 486].—α-2 : 5 : 3-*Dimethylethylpiperazine* boils at 176° and is difficult to obtain free from water; when cooled with ice, it solidifies to a colourless, crystalline mass. The *dibenzoyl* derivative crystallises in colourless, lustrous tablets, and melts at 169°.

β-2 : 5 : 3-Dimethylethylpiperazine boils at 185—186°, and, like the α-base, cannot readily be obtained quite free from water. It does not solidify at 0°; the *hydrochloride* is readily soluble in alcohol and crystallises with difficulty; the *platinochloride* crystallises with $2H_2O$ in lustrous plates; the *picrate,* which crystallises with $\frac{1}{2}H_2O$, melts and decomposes at 250°. The dinitrosamine and dibenzoyl derivative were obtained as oily liquids.

IV. [With P. BRANDES; compare Abstr., 1896, i, 576].—*α-Tetramethylpiperazine* (compare Wolff, Abstr., 1893, i, 373) crystallises in colourless, slender needles, boils at 177°, and melts at 37°; the *hydrochloride* is very sparingly soluble in alcohol. The *dinitrosamine* crystallises in colourless prisms and melts at 157°. The *dibenzoyl* derivative crystallises in colourless, lustrous tablets, and melts at 242°. The *picrate* and the *mercurochloride* are sparingly soluble in water.

β-Tetramethylpiperazine boils at 181° and could not be obtained in the solid form; the *hydrochloride* is moderately soluble in alcohol and forms slender needles. The *dinitrosamine,* which crystallises in small colourless needles, can be sublimed without decomposition and melts at 101°. The *dibenzoyl* derivative crystallises in colourless, lustrous prisms melting at 175°. A. H.

Cinnoline. By MAX BUSCH and ALBERT RAST (*Ber.*, 1897, **30**, 521—527. Compare Busch and Klett, Abstr., 1892, 1494, and von Richter, Abstr., 1883, 1105).—*Dihydrocinnoline,* $C_6H_4<\begin{matrix}CH:CH\\NH\cdot NH\end{matrix}$, is best obtained by dissolving 5 grams of chlorocinnoline (*loc. cit.*) in 100 grams of sulphuric acid (15 per cent.) and then adding 5 grams of iron filings; the mixture is kept well shaken, and the reduction is complete at the end of 2 hours. Any filings that may be left are filtered off, the filtrate rendered neutral with solid soda, and then extracted several times with ether; the yellow crystals obtained by distilling off the greater part of the solvent are recrystallised from light petroleum. The substance crystallises in colourless plates, melts at 87—88°, and can be distilled without undergoing decomposition. It is but slightly basic, its salts being instantaneously decomposed by water, and it has an odour somewhat similar to that of naphthylamine. Reducing agents have no action on the base. The *hydrochloride,* $C_8H_8N_2,HCl$, crystallises from its concentrated alcoholic solution in flat, glistening needles, melts and decomposes at 149—150°, and when not quite pure readily turns brown on exposure to the air. No platinochloride could be obtained. The *sulphate,* $C_8H_8N_2,H_2SO_4$, resembles the hydrochloride.

Cinnoline (*α-phenoiazine*), $C_6H_4<\begin{matrix}CH:CH\\N{=}N\end{matrix}$, is best obtained by oxidising dihydrocinnoline (1 part) dissolved in benzene with freshly prepared mercuric oxide (20 parts); as the oxidation takes place but slowly, it is necessary to warm the mixture for 3 hours on the water bath. The base is best purified by means of its *hydrochloride,* which separates in green or brownish, glistening needles on adding ether to the alcoholic solution; it is readily soluble in water and alcohol, begins to sublime at 100°, softens at 156°, and melts at 160°. The *base* is

obtained as an oil on adding sodium hydroxide to the hydrochloride. In the cold, it crystallises from light petroleum in small, glistening, compact crystals which melt at 39°, and from ether in colourless, glistening needles which contain 1 molecule of ether of crystallisation and melt at 24—25°. Cinnoline is a strong base, and is readily soluble in most solvents, even in water. It possesses a characteristic odour somewhat resembling that of geraniums, has an extremely bitter taste, is poisonous, and decomposes slightly when distilled.

The *picrate*, $C_8H_6N_2,C_6H_2(NO_2)_3\cdot OH$, crystallises in amber-yellow prisms, melts at 190°, and is sparingly soluble in alcohol but insoluble in water. The *platinochloride*, $(C_8H_6N_2)_2,H_2PtCl_6$, which is obtained as a yellowish, crystalline precipitate, decomposes at 280°. The *aurochloride* crystallises in dark yellow needles and melts at 146°. *Cinnoline methiodide*, $C_8H_6N_2,CH_3I$, crystallises in glistening, reddish-brown needles and melts at 168°. J. J. S.

Methylanthranilic Acid and some Quinazoline Derivatives. By G. FORTMANN (*J. pr. Chem.*, 1897, [ii], **55**, 123—136).—Methylanthranilic acid (Zacharias, Abstr., 1891, 912) is best prepared by heating anthranilic acid with caustic potash and methylic iodide. The *copper* salt crystallises with $1H_2O$. *Nitrosomethylanthranilic acid* forms yellowish crystals melting at 128°. The corresponding *hydrazine*, which can only be obtained with difficulty and in small quantity, forms white crystals melting at 120°. *Acetomethylanthranilic acid* is a white, crystalline powder melting at 186°. *Benzomethylanthranilic acid* melts at 161°. Methylanthranilic acid readily reacts with phenylcarbimide, forming 3′ : 1′-*phenylmethyldiketoquinazoline*,

$$C_6H_4<\begin{matrix}CO-NPh\\ \quad\ \ | \\ NMe\cdot CO\end{matrix},$$

which crystallises in white needles melting at 233°. It is an indifferent substance, and appears not to yield salts. Ethylcarbimide does not yield a quinazoline derivative with the acid, but complete decomposition occurs when it is heated. Paratolylcarbimide yields 3′: 1′-*tolylmethyldiketoquinazoline*, which crystallises in slender, white needles melting at 254°. With phenylthiocarbimide, the acid yields 3 : 1′-*phenylmethylthiodiketoquinazoline*, $C_6H_4<\begin{matrix}CO-NPh\\ \quad\ \ | \\ NMe\cdot CS\end{matrix}$, which melts at 288—289°, and does not yield salts.

1′ : 3′-*Dimethylthiodiketoquinazoline*, obtained by the use of methylthiocarbimide, melts at 186°; when heated with mercuric oxide and water, it is converted into 1′: 3′-dimethyldiketoquinazoline, melting at 151° (Abt, Abstr., 1889, 639). The corresponding allyl derivative could not be obtained. Phenylcarbimide unites with acetylanthranilic acid to form an *additive* compound which melts at 175°. The corresponding *benzoyl* derivative melts at 175°. Ethylcarbimide and phenylthiocarbimide, on the other hand, do not appear to combine with acetyl- and benzoyl-anthranilic acids. A. H.

Imidomethyloxytriazine. By ADRIANO OSTROGOVICH (*L'Orosi*, 1896, **19**, 397—402; also *Gaz*, **27**, i, 222—228. Compare Abstr., 1896, i, 262).—On heating acetylurethane with guanidine carbonate

in a sealed tube for 6 hours at 135—140° and washing the solid product with alcohol, guanidine carbonate is extracted, leaving a residue of *imidomethyloxytriazine carbonate*, $(C_4H_6N_4O)_2,H_2CO_3$, which crystallises in small pyramids and is decomposed by boiling with water.

Imidomethyloxytriazine, $NH<\begin{matrix}CMe:N\\CO\cdot NH\end{matrix}>C:NH$, is best prepared by treating a boiling solution of the hydrochloride or sulphate with sodium carbonate, when it separates slowly as a white, crystalline powder which, on heating, decomposes without melting. The *hydrochloride*, $C_4H_6N_4O,HCl$, is crystalline and very soluble, whilst the *sulphate*, which crystallises with $3H_2O$ in hard, white prisms, is sparingly soluble in water. The *picrate* blackens at 260°, and is not explosive, whilst the *silver* salt, $C_4H_5N_4OAg$, is a white powder which yields alkylic derivatives when treated with alkylic iodides.

W. J. P.

A New Synthesis of Phenylated Tetrazo-derivatives. By EDGAR WEDEKIND (*Ber.*, 1897, **30**, 449—451).—Nitrous acid reacts with guanazylbenzene on warming, with the formation of a compound identical with the diphenyltetrazole obtained from parahydroxytriphenyltetrazoliumchloride.

The same compound is produced when guanazylbenzene is treated with nitric acid at a moderately high temperature. J. F. T.

Derivatives of Benzoparathiazines [Phenoparathiazines]. By OSKAR UNGER (*Ber.*, 1897, **30**, 607—610).—When bromacetic acid is brought into contact with amidothiophenol, *ketodihydrophenoparathiazine*, $C_6H_4<\begin{matrix}NH\cdot CO\\S-CH_2\end{matrix}$, is quantitatively formed; this crystallises in long, white needles, melts at 179°, and dissolves in concentrated hydrochloric acid and in aqueous potash. Bromacetic bromide, on the other hand, enters into reaction with two molecules of amidothiophenol, forming the *hydrobromide of a base*, $C_{14}H_{15}N_2OS_2Br$, which melts at 197°. Its alcoholic solution is decomposed by water, the free *base*, $C_{14}H_{14}N_2OS_2$, being precipitated in slender needles melting at 88—89°; the constitution of this substance has not yet been ascertained. With ω-bromacetophenone, amidothiophenol yields *phenylphenoparathiazine*, $C_6H_4<\begin{matrix}N:CPh\\S\cdot CH_2\end{matrix}$, which crystallises in light, sulphur-yellow cubes melting at 233°. It is not affected by acetic anhydride or nitrous acid, but hydriodic acid and phosphorus reduce it to aniline, hydrogen sulphide, and an oil which is probably ethylbenzene. Ethylenic bromide, when heated with amidothiophenol, yields the hydrochloride of the ethylene ether of amidothiophenol; the *base* itself melts at 82°. When the solution of amidothiophenol in ethylenic bromide is heated with hydrochloric acid at 150—160°, the *bromethyl ether*,

$$NH_2\cdot C_6H_4\cdot S\cdot CH_2\cdot CH_2Br,$$

is formed as an oil which volatilises slowly with steam. A. H.

Stearates of the Alkaloids and their Therapeutic Application. By FRANCESCO ZANARDI (*Chem. Centr.*, 1896, i, 765; from *Boll. chim. farm.*, 1896, 4).—*Morphine stearate*, $C_{17}H_{19}NO_3,C_{17}H_{35}\cdot COOH$, prepared

by slowly adding morphine to an alcoholic solution of stearic acid, forms crystals which can be dried at 30—40°. It is also obtained on mixing aqueous solutions of sodium stearate and morphine hydrochloride, as a voluminous mass which, on recrystallisation from alcohol, forms white, pearly scales melting at 84—86°. It is easily soluble in hot alcohol, slightly so in ether and in cold alcohol, and also in oils to the extent of about 1 per cent., and in fats and vaselin.

Atropine stearate, $C_{17}H_{23}NO_3,C_{17}H_{35}\cdot COOH$, which is prepared in a similar way to the morphine salt and resembles it also as regards solubility, crystallises in white, pearly needles, and melts at 120°. A solution of 0·1 gram in 50 grams of almond oil is a suitable substitute for the oils of henbane and belladonna.

Cocaine stearate, $C_{17}H_{21}NO_4,C_{17}H_{35}\cdot COOH$, is prepared in a similar manner to the preceding salts, and resembles them as regards solubility. It crystallises in white needles, and melts at about 90°.

The presence of stearic acid in these stearates was proved by means of copper sulphate, and the alkaloids were identified by their characteristic reactions. E. W. W.

Morphine Methohydroxide. By EDUARD VONGERICHTEN (*Ber.*, 1897, **30**, 354—357).—The loss of water which crystallised morphine methohydroxide, $C_{17}H_{19}NO_3,MeOH + 5H_2O$, has long since been observed to undergo at 100° corresponds best with the formation of an intramolecular anhydride, which would be a hydrogenised phenolbetaine, $C_{16}H_{15}O_2{<}\genfrac{}{}{0pt}{}{O}{NMe_2}{>}$. Morphine methiodide was converted, by successive treatment with silver sulphate and barium hydroxide, into the methohydroxide, and this was found to unite with methylic iodide in methylic alcoholic solution, yielding codeine methiodide, convertible into methylmorphimethine by boiling with aqueous sodium hydroxide. Codeine methiodide would then have the constitution

$$OMe\cdot C_{16}H_{15}O_2{:}NMe_2I.$$

It is thought that this view of the relationship of the two substances satisfactorily explains the striking differences observed between the methiodides and methohydroxides of codeine and morphine respectively. C. F. B.

Aconitum Septentrionale (Koelle). By H. V. ROSENDAHL (*J. Pharm.*, 1896, [vi], 4, 262—266).—This plant has yielded the three alkaloids, lapaconitine, septentrionaline and cynoctonine. *Lapaconitine*, $C_{34}H_{48}N_2O_8$, occurs in well-developed crystals, probably hexagonal; it melts at 205°, is soluble in 126 parts of alcohol, 330 parts of ether, or 1472 parts of water; the solutions of the alkaloid and of its salts are dextrogyrate and possess a reddish-violet fluorescence. A *tribromo*-derivative was obtained. When warmed with alkalis, lapaconitine yields an alkaloid melting at 98°, and readily soluble in ether; an alkaloid sparingly soluble in ether, and melting at 106°; and a crystalline acid melting at 114° and free from nitrogen.

Septentrionaline, $C_{31}H_{48}N_2O_9$, which is a yellowish powder melting at 128·9°, acts as an anæsthetic. Its solutions and those of its salts are dextrogyrate and non-fluorescent; it is readily soluble in alcohol and

ether, but only moderately so in water. It yields a *tribromo*-derivative, and on warming with alkalis is converted into an alkaloid readily soluble in ether (m. p. 88°); an alkaloid sparingly soluble in ether (m. p. 105°); and the same acid as that obtained from lapaconitine.

Cynoctonine, $C_{36}H_{55}N_2O_{13}$, is an extremely hygroscopic, amorphous alkaloid, and readily decomposes. It is readily soluble in alcohol, moderately in water, and extremely sparingly in ether. It melts at 137°, and its solutions are dextrorotatory but non-fluorescent. With sulphuric acid, it gives a reddish-brown coloration, and if evaporated just to dryness in the presence of fuming nitric acid, it yields a residue, which on treatment with alcoholic potash gives a blood-red coloration. A *tribromo*-derivative has been obtained. The physiological actions of the three alkaloids are given in some detail, and the paper concludes with a summary of the alkaloids obtained from different species of aconite, together with a description of their properties. J. J. S.

Ketones of the Tropine Group, VII. Dibenzylidenetropinone. By RICHARD WILLSTÄTTER (*Ber.*, 1897, **30**, 731—736).—*Dibenzylidenetropinone*, $C_8H_9NO(CHPh)_2$, is formed when benzaldehyde is condensed with tropinone in the presence of hydrochloric acid. It crystallises from absolute alcohol in transparent, yellow prisms melting at 152°; the *hydrochloride* forms glistening, light-yellow prisms and needles melting and decomposing at 270—271°; the *phenylhydrazone* crystallises from alcohol in glistening, pleochromatic needles melting at 193°, and the *methiodide* forms silky needles melting and decomposing at 264—265°. J. F. T.

Synthesis of the Hæmoglobins. By WILHELM PREYER (*Ber.*, 1897, **30**, 190—191).—The author points out that, contrary to the statement of Nencki (*Ber.*, 1896, **29**, 2878), synthesised hæmoglobin has been obtained in crystals (Preyer, *Die Blutkrystalle*, p. 137, Jena, 1871). A. H.

Properties of the Alcohol-soluble Proteid of Wheat and of certain other Cereal Grains. By G. L. TELLER (*Amer. Chem. Journ.*, 1897, **19**, 59—69).—A 1 per cent. salt solution extracts more nitrogenous matter from wheat flour than do stronger solutions (10 per cent. and 15 per cent.), the difference being due to such compounds as are not precipitated from the solution when alcohol is added until it contains 75 per cent. The filtrate from such a solution gives the characteristic proteose reactions, as well as the biuret reaction for proteids.

Careful estimations of the proteids soluble in alcohol extracted from wheat by 1 per cent. salt solution show that, after subtracting the amidic nitrogen, the amount of such proteid present contains 0·27—0·30 per cent. of nitrogen on the wheat taken, and is almost constant in the samples of wheat which were examined; this proteid is probably gliadin. The solubility of this substance indicates another source of inaccuracy in the estimation of the gluten in wheat by washing. It appears that the proteoses which have been found in the aqueous or dilute salt extracts of wheat, barley, oats, and rye are in reality the proteids soluble in alcohol. (Compare Chittenden and Osborne, *Amer. Chem. Journ.*, **13** and **14**). A. H.

Organic Chemistry.

Action of Nickel on Ethylene. By PAUL SABATIER and JEAN B. SENDERENS (*Compt. rend.*, 1897, **124**, 616—618).—Nickel reduced from the oxide by hydrogen and allowed to cool in a current of the gas has no action on ethylene at the ordinary temperature, but at about 300°, and still more readily at a somewhat higher temperature, the nickel gradually intumesces and yields a very bulky black product, which is a mixture of nickel and carbon. The reaction is most rapid when the metal has been reduced at a low temperature (about 300°), but it takes place readily even if the metal has been reduced at a red heat. If the layer of reduced metal is about 20 cm. long, the ethylene is completely decomposed, and the issuing gas is a mixture of methane with from 10 to 50 per cent. of hydrogen, according to the temperature at which the reaction takes place, the proportion of hydrogen being higher the higher the temperature. Minute traces of higher hydrocarbons of the methane series also seem to be formed. The main reaction is probably $C_2H_4 = C + CH_4$, the liberation of hydrogen being due to a secondary reaction which takes place under conditions not yet well defined.

A relatively small quantity of nickel will decompose a large quantity of the gas. The reaction can scarcely be attributed to absorption of the ethylene by porous metal, because the decomposition takes place with nickel filings, although less regularly and at a higher temperature. No similar decomposition takes place with finely-divided iron, cobalt, copper, platinum, or palladium, and in this respect the change differs from the decomposition of acetylene as observed by Moissan and Moureu (Abstr., 1896, i, 585). It is possible that an unstable compound of nickel and ethylene is first formed and afterwards splits up into nickel, carbon, and methane.

Ethylene acts on nickel oxide at a comparatively low temperature, and the phenomena will be described subsequently. C. H. B.

Decomposition of Hexane and Trimethylethylene by Heat. By FRITZ HABER (*Chem. Centr.*, 1896, ii, 237—240; 377; from *J. Gasbel*, **34**, 377—382, 395—399, 435—438, 452—455).—From his researches on acetylene, Berthelot regarded the reactions occurring in the flame as consisting of decomposition of hydrocarbons with liberation of hydrogen, recombination of these products, and union of simpler hydrocarbons to form denser ones. Between these processes of decomposition and combination, a complicated state of equilibrium was supposed to be established. To these views the author raises the following objections. It is entirely unproved that all the hydrocarbons result from the repeated splitting off of hydrogen and condensation of the residues. At high temperatures, direct decomposition into carbon and hydrogen, with immediate polymerisation of the atoms of the former, may also occur. The theory of equilibrium is only based on a qualitative proof of a series of hydrogen-additions and hydrogen-eliminations in the case of some simple hydrocarbons (acetylene,

ethylene, methane, and amylene), and the enormous number of compounds which should result according to this theory have never been observed. The importance of acetylene in this series of equilibria is not intelligible, since, according to Berthelot's experiments, it is only present in very limited quantity, and, moreover, it readily forms aromatic compounds, whilst on heating with hydrogen, ethylene is produced in very variable quantity according to the conditions, and on heating with ethylene, it only yields some crotonylene.

In opposition to Lewes' theory of the luminosity of flame (Trans., 1892, 322), the author points out that tarry substances, formed by the polymerisation of decomposition products, are found, not only in the luminous, but also in the non-luminous zone of the flame, and as long as it is not proved that these tarry substances decompose into acetylene before being resolved into carbon and hydrogen, Lewes' theory of the luminosity being caused exclusively by the decomposition of acetylene is untenable (compare A. Smithells, Trans., 1892, 204). Haber has chosen normal hexane for experiment for the following reasons: (1) Because it is susceptible of decomposition into lower hydrocarbons, for example, $C_6H_{14} = C_5H_{10} + CH_4$, in a way which is impossible in the case of simpler hydrocarbons, such as methane, ethane, &c.; (2) because it can be partially decomposed by exposure for a short time to an incipient red heat, whilst the lower hydrocarbons require a high temperature, which renders it impossible to isolate the products of decomposition in their primary form; (3) because a direct conversion into aromatic compounds, as suggested by Armstrong and Miller, in the case of higher aliphatic compounds, could especially easily take place in the case of this six-carbon hydrocarbon; (4) because hexane being the chief component of commercial gasoline, a knowledge of its decomposition products is of great importance.

The experiments showed that hexane and trimethylethylene decompose into smaller molecules without liberation of hydrogen. In the aliphatic series, the union of carbon and hydrogen atoms is stronger than that of carbon with carbon, whilst in the aromatic series the reverse is the case, hence the stability of benzene and solid hydrocarbons containing one or two carbon atoms as compared with the ready decomposition of the higher aliphatic compounds; in this connection, the author quotes the researches of Breitenlohner, Vohl, Thorpe and Young. A second regularity was shown in the fact that by superheating the vapours of hydrocarbons at a high temperature for a short time, a portion was simply split off from the end of the carbon chain with some rearrangement of the hydrogen atoms in such a way that the larger residue always contained a double bond when the original hydrocarbon possessed none. Apparently, hydrocarbons with less than three carbon atoms are split off, and it depends on the conditions as to whether these are methane, ethane, ethylene, or acetylene. The reaction lying at the basis of this decomposition is shown by heating hexane for about two seconds to 600—800°, when very little formation of hydrogen takes place, and the addition of hydrogen to the olefines is also insignificant, because at this temperature the union of hydrogen, even with acetylene, is very slow. Trimethylethylene behaves very similarly to hexane, but the heavier

product of decomposition unites with other molecules to form more complex hydrocarbons.

There is no equilibrium established between the reactions of decomposition and recombination, but the latter are of an altogether different character to the former. Between 900° and 1000°, secondary reactions become more evident, and even in the case of hexane, at this temperature the primary decomposition products are not all stable. By continued splitting off of terminal portions of the chain, more complex tarry substances are formed and hydrogen is liberated in noticeable amount, the decomposition of the lowest members of the different series (Berthelot and Lewes' special case) beginning to take place alongside the decomposition of the original material. At this point, the liberated gases contain hydrogen, methane, ethylene, benzene, and traces of other hydrocarbons. From a mathematical examination of the analytical results, the author infers that a portion of the products of decomposition at lower temperatures which has been held to contain homologues of methane, consists in reality of compounds containing less hydrogen, very similar to the paraffin group and possibly belonging to the trimethylene series. Direct formation of benzene from hexane was not proved, and the fact that both hexane and trimethylethylene give the same yield of benzene, indicates that this hydrocarbon is formed exclusively from acetylene. From a comparison of the weights of gaseous olefines and benzene obtained in the various decompositions, it is seen that, at a dark red heat, the carburation value of the products depends essentially on the olefines. At 900—1000°, on the other hand, the carburation value is only half, owing to the greater quantity of benzene. In practice, the conditions for the formation of benzene are more unfavourable, but in spite of this, the gas from gasoline at a high temperature showed that a certain proportion of the carburation value was to be ascribed to benzene. At 900—1000°, benzene becomes unstable, and hence its formation from hexane and trimethylethylene decreases.

[With H. SAMOYLOWICZ].—*Decomposition of Hexane.*—Details are given of the methods employed in analysing the products of the decomposition.

In order to ensure that the gas was uniformly heated throughout, coils of narrow glass combustion tubing were used, being heated in baths of sulphur (448°), phosphorus pentasulphide (518°) or stannous chloride (606°). When zinc chloride was used, a brass coil was employed. This was freely suspended in a steel crucible round which a second steel crucible was fitted, the space between containing the chloride. The inner crucible was closed by a porcelain lid through a hole in which the ends of the coil, protected by means of a porcelain tube, passed. For heating purposes, a small muffle or an asbestos fire-clay furnace was used. In some cases, air baths consisting of iron crucibles with fitted conical tops were employed, the coil wrapped in asbestos being suspended in the lower vessel and the temperature ascertained by means of the Prinsep's alloy contained in the asbestos covering. The vaporisation of the hexane was effected by slowly admitting the liquid into a flask heated at 100° to which a delivery tube leading to the decomposition coil was attached. The coil was connected suc-

cessively with a condenser and a distilling flask, both immersed in a mixture of ice and salt, the latter serving as a reservoir for the collection of tar, then came a Winkler's coil cooled by ice, a second coil for condensation of paraffin oils, and finally the gas reservoir, a vessel of 69 litres capacity with a stopper fitted with thermometer, gas-delivery tube, water exit pipe, and manometer. The flow of water was regulated by varying the length of the longer arm of the siphon.

Hexane remains unchanged if heated for a short time at 518°, but at 606° the decomposition is very considerable, olefines and paraffins being the main products with some hydrogen and benzene, which is indicative of rupture of the carbon chain in such a way that, from one molecule of hexane, one molecule of an olefine and one of a paraffin are formed. Of the paraffins, methane is the most abundant, constituting at least 70 per cent., hence the decomposition consists essentially in the splitting off of a terminal CH_3 group with formation of amylene and methane. The small amount of liquid olefines in comparison with the gaseous olefines and the mean molecular weight of the latter, namely 39, indicate that amylene undergoes a secondary decomposition to some extent into ethylene and propylene. Acetylene, hydrogen, and carbon result from an insignificant bye-reaction whose nature was not determined. Two experiments at 730° and 820° showed a similar decomposition. In one experiment, direct proof of the presence of propylene, amylene, and ethylene was obtained by employing a coil containing fuming sulphuric acid, which absorbs the two former with ease and the last only with difficulty. In all these experiments, the separation of carbon was extremely small, but at temperatures from 1190—1220° the separation was so great that the cast iron heating tubes of 10 mm. bore were soon choked. The greater portion of the hexane was decomposed into its elements and there was no condensation of tar. Besides hydrogen (65·2 per cent.) the only hydrocarbon found in considerable quantity (22·6 per cent.) was methane, acetylene occurring only in traces.

The gases obtained at temperatures up to 820° were photometrically examined. Hexane was found to be one of the best materials for the production of oil gas. This substance furnishes a gas which, "after cooling to – 10° and washing with paraffin oil at 0°, possesses a candle power of 61·5—74·5 English candles per consumption of 5 cubic feet and of 186·5—198 candles per kilogram of original material." Tar consisting of a mixture of unchanged hexane and amylene is also produced to the extent of 37—48 per cent. The value of hexane and similar materials for the production of gas has been hitherto far underestimated, as they have been tried under unfavourable conditions, producing a gas containing only 30 per cent. of olefines instead of, as in this case, 50 per cent. E. W. W.

Derivatives of Diamylene and of Isodibutylene. By IWAN ROBERT SCHINDELMEISER (*Chem. Centr.*, 1896, ii, 354; from *Diss. Dorpat*, 1896).—Halogen compounds were prepared from both hydrocarbons, and alcohols possessing a peculiar, putrid, musty odour were obtained from the iodides. On decomposition with alcoholic potassium hydroxide, diamylenic chloride re-forms diamylene, whilst isodibutylene

chloride gives, not only isobutylene, but also a hydrocarbon, which results probably from the displacement of the hydroxyl group by chlorine, and which has an odour similar to that of isodibutol.

E. W. W.

Action of Acetylene on Cupric Salts. By HENRIK G. SÖDERBAUM (*Ber.*, 1897, 30, 760—765).—The action of acetylene on cupric salts seems to have been for the most part disregarded, although on passing a stream of the pure gas into an ammoniacal solution of either cupric sulphate or nitrate, a black, flocculent precipitate is slowly produced.

This substance, after being dried over sulphuric acid, gave various results on analysis, a fact which was found to be due to the absorption of oxygen from the air during the process of drying; in an exhausted desiccator, however, the substance ceased to increase in weight after 2 days, and then yielded, on analysis, numbers corresponding with the formula $(C_{17}Cu_8H_4O_3)_n$. This *copper acetylide* is a black, amorphous powder insoluble in water and organic solvents; it explodes between 70° and 80° when heated, and decomposes quickly on heating with hydrogen chloride with formation of the halogen salt of copper, and a carbonaceous residue of the formula $(C_{12}H_4O_3)_n$; this is probably similar to the graphite hydrate obtained by Schützenberger and Bourgeois from crude iron.

On passing acetylene into a neutral or faintly acid solution of copper acetate, a precipitate is formed corresponding in composition with the formula $(C_8Cu_4O)_m + (H_2O)_n$, and differing from the compound above mentioned in being stable in the air and non-explosive. It seems, therefore, from these experiments, that a large number of copper acetylides are capable of existing.

J. F. T.

Action of Acetylene on Cupric Salts. By HENRIK G. SÖDERBAUM (*Ber.*, 1897, 30, 814—815).—The composition of the precipitate produced by acetylene in a dilute ammoniacal solution of copper sulphate varies with the temperature at which the precipitation is effected. At +5°, the compound, after drying over phosphoric anhydride, has the composition $C_{24}H_2Cu_{12}O$ ($= 12C_2Cu + H_2O$), and is a black powder, which explodes at 50° when quickly heated, and is dissolved by potassium cyanide and dilute sulphuric and hydrochloric acids, a small amount of a carbonaceous residue being invariably left. At 15°, the acetylide contains less copper, whilst the amount of carbon remains practically unaltered. The atomic ratio of carbon to copper, therefore, is at this temperature greater than 2 : 1.

A. H.

Magnesium Methoxide. By EMERICH SZARVASY (*Ber.*, 1897, 30, 806—809).—*Magnesium methoxide*, $Mg(OMe)_2$, is formed when perfectly bright magnesium ribbon is placed in absolute methylic alcohol at the ordinary temperature and when the two are heated together; if the solution thus formed contains about 6 grams of magnesium to 40 grams of methylic alcohol, transparent, pointed prisms are deposited, which contain 3 mols. methylic alcohol, effloresce rapidly in the air, and are soluble in ethylic alcohol and in benzene. From more concentrated solutions, the methoxide separates as an amorphous mass and is de-

posited as an amorphous powder when its solutions are heated. When treated with water, it yields magnesium hydroxide and methylic alcohol, and when heated in a vacuum, it decomposes, evolving a mixture of carbonic anhydride, carbonic oxide, and hydrogen. Bromine converts it into bromoform and magnesium bromide. A. H.

Reaction of Mercaptides with Alkylic Iodides.—By KARL A. HOFMANN and W. O. RABE (*Zeit. anorg. Chem.*, 1897, **14**, 293—296).—Hydrogen platinochloride, when treated with ethylic mercaptan in alcoholic solution, yields platinic mercaptide, $Pt(SEt)_4$, which, when allowed to remain in a vacuum at 100°, is quickly converted into platinous mercaptide. The latter, when heated with ethylic iodide in a pressure flask for 2 days at 70° to 80°, yields the compound $Pt(Et_2S)_2I_2$, which separates in large, red crystals, melts at 137°, and is identical with Blomstrand's platosoethylsulphine iodide obtained from platinum iodide and ethylic sulphide. Methylic iodide reacts with platinous mercaptide more quickly than ethylic iodide, and yields the compound $Pt(SEtMe)_2I_2$ which melts at 98°; this, when treated with silver nitrate in alcoholic solution yields all its iodine as silver iodide at the ordinary temperature.

Palladium chloride and ethylic sulphide yield the compound $Pd(SEt)_2$. Iridium sesquichloride yields the compound $Ir(SEt)_2$.

Mercury mercaptide when treated with ethylic iodide for 24 hours at the ordinary temperature, and then at 40° to 50°, yields the double compound HgI_2,SEt_3I; this crystallises in yellow needles, melts at 107°, and when treated with hydrogen sulphide in alcoholic solution is decomposed into red cinnabar and triethylsulphine iodide. The corresponding methyl compound, HgI_2,SMe_3I, crystallises in large, yellow plates, melts at 160°, and when treated with dilute nitric acid yields free iodine, and after prolonged boiling, mercury iodide. E. C. R.

Allylic Phosphates. By JACQUES CAVALIER (*Compt. rend.*, 1897, **124**, 91—92).—In a former communication (Abstr., 1895, i, 638), the preparation of allylphosphoric acid, $C_3H_5H_2PO_4$, by the action of phosphoric anhydride on allylic alcohol in ethereal solution was described. The mother liquors from the barium salt of this acid yield, on evaporation, the barium salt of diallylphosphoric acid, $(C_3H_5)_2HPO_4$, as a gelatinous mass. This can be converted into the *lead* salt, $[(C_3H_5)_2PO_4]_2Pb$, crystallising in fine, colourless needles. *Triallylic phosphate*, $(C_3H_5)_3PO_4$, is prepared by the action of triargentic phosphate on allylic iodide, but is difficult to purify. When boiled with barium hydroxide and water, it yields barium diallylphosphate. Diallylphosphoric acid is stable in aqueous solution in the cold, but when warmed it yields first allylphosphoric acid and then phosphoric acid. The diallylphosphates are much more stable in solution than the acid itself. The sodium and potassium salts are deliquescent, and crystallise with difficulty; the salts of calcium, barium, lead, and silver crystallise without water and are very soluble. Lead diallylphosphate melts at 151°, and when heated to 200° decomposes into triallylic phosphate which vaporises, and lead allylic phosphate which burns at a higher temperature, lead pyrophosphate alone remaining. The silver salt behaves in a similar manner.

When the calcium salt is heated to a high temperature, it decomposes, leaving a residue of calcium metaphosphate. A. C. C.

Separation of Galactose and Arabinose. By EUNM SUBASCHOW (*Chem. Centr.*, 1896, ii, 134—135; from *Zeit. Ver. Rübenzuck-Ind.*, 1896, 270—273).—*Galactosebenzhydrazide*, $C_{13}H_{18}N_2O_6,H_2O$, is prepared by digesting a mixture of 1 part of galactose with the calculated quantity of benzhydrazide and 20—25 parts of 96 per cent. alcohol on the water bath. After $1\frac{1}{2}$—2 hours, the whole mass is liquid, and on cooling some galactosebenzhydrazide separates out, but the main portion only after evaporating down to one-third or one-fourth. After crystallisation from alcohol, this compound forms long, white, rectangular plates, melts at 78° becoming brown, and is slightly soluble in cold water, easily in hot water with partial decomposition, very soluble in hot 96 per cent. alcohol, and slightly so in the cold.

Arabinosebenzhydrazide is prepared in a similar way; the arabinose dissolves almost instantaneously, and in 15—20 minutes the hydrazide, $C_{12}H_{16}N_2O_5$, begins to separate, and after boiling half-an-hour and cooling is completely deposited. After crystallisation from alcohol, it forms white, silky plates, melts and decomposes at 184°, and is very slightly soluble in cold water, easily in hot, with partial decomposition, almost insoluble in cold 96 per cent. alcohol, very slightly soluble on boiling, and more easily so in dilute hot alcohol. Arabinosebenzhydrazide may also be prepared by digesting cherry-gum with dilute sulphuric acid and subsequently treating with benzhydrazide. With benzaldehyde in alcoholic solution, it forms benzylidenebenzhydrazide.

The separation of arabinose from galactose depends on the different rates of formation of their benzhydrazides and their different solubilities. For example, 200 grams of gum arabic, a sample of which, on oxidation with nitric acid, gave a large quantity of mucic acid, was digested with 400 grams of 6 per cent. hydrochloric acid on the water bath for 6 hours. After neutralisation with lead carbonate and decolorisation with bone charcoal, the filtrate was evaporated to 75 c.c., when it yielded a syrup of density 1·168, which was treated with 10 grams of benzhydrazide and 75 grams of water. After remaining a day at the ordinary temperature, a precipitate was formed which, when purified, melted at 184°. E. W. W.

Carbohydrates in Beer. By PAUL PETIT (*Compt. rend.*, 1897, 124, 510—511).—Beer that has been kept in a cool place for 3 months contains half of its extractive matter in the form of dextrin, containing about 3·6 per cent. of pentoses. Its rotatory power is $\alpha_D = 149·6°$, and its reducing power 13·4 per cent. in terms of maltose, and 6·3 per cent. in terms of glucose. In several ways, it behaves differently from ordinary dextrin; it is less readily inverted by hydrochloric acid, but the hydrolysis proceeds further, and is not limited by the formation of dextrose; it is also less readily converted into brown products by the prolonged action of the acid.

When heated with diastase for an hour at 52°, with yeast for 3 days at 27°, and with a mixture of diastase and yeast for 3 days at 27°, the beer dextrin yields the following results:

	Rotatory Power.	Reducing Power. (Maltose.)
Initial	149·6°	13·4
With diastase	125·3	18·7
With yeast	106·5	10·5
With yeast and diastase	32·1	4·7

It is noteworthy that, after the combined action of yeast and diastase, and after the action of hydrochloric acid for 3 hours, the products from the beer dextrin have practically the same rotatory powers, whilst the rotatory power after fermentation with yeast alone is practically identical with that observed after the action of hydrochloric acid for an hour and a quarter, the latter being the time required for the conversion of ordinary dextrin into dextrose under the same conditions. C. H. B.

Action of Iodine on Starch. By GASTON ROUVIER (*Compt. rend.*, 1897, **124**, 565—566).—If it is supposed that, in the action of iodine on starch when the former is in excess, but not in sufficient quantity to form the compound $(C_6H_{10}O_5)_{16}I_5$ (Abstr., 1894, i, 353), the compounds $(C_6H_{10}O_5)_{16}I_3$ and $(C_6H_{10}O_5)_{16}I_4$ are formed and have the power of dissolving a further quantity of iodine, it seems probable that the proportion of iodine dissolved by one or other of them will depend on the concentration of the iodine in the supernatant liquid in accordance with the law of Berthelot and Jungfleisch concerning the partition of a soluble substance between two non-miscible solvents. This view is confirmed by a close agreement between the observed and calculated numbers. C. H. B.

A Third Diastase-Achroodextrin and the Isomaltoses. By EUGEN PRIOR (*Chem. Centr.*, 1896, ii, 86 ; from *Centr. Bakt. Parasitenk*, **2**, [Abtlg. II], 271—273).—The author has examined the products obtained by the incomplete saccharification of potato starch by green malt according to the method of Lintner and Düll. From the mixture, which still shows the erythrodextrin reaction, the easily fermentible sugars and the greater portion of the maltose were removed by fermentation with Saaz yeast. The residue, which must contain Bau's β-isomaltose, when treated with alcohol of various strengths and fermented a second time, yielded the third dextrin, which has approximately a rotatory power of 173° and a cupric-reducing power of 53·7 (maltose = 100). This dextrin is distinguished from achroodextrin I and II by its fermenting with difficulty with the Frohberg and Saaz yeasts, being attacked by the former more than by the latter under the ordinary conditions at 25°, but it is completely decomposed by both in the author's vacuum apparatus. By mixing this dextrin with about 20 per cent. of pure maltose and treating the product with phenylhydrazine acetate, no trace of maltosazone could be obtained, but the osazone of melting point 150—152° which has been hitherto regarded as the characteristic isomaltosazone is formed. The mixture of dextrins obtained from the residue after fermentation and insoluble in 80 per cent. alcohol, behaves similarly when mixed with maltose. The author therefore regards the isomaltoses principally as mixtures of achroodextrin III and maltose, but is yet uncertain as to whether the former is identical with Lintner and

Düll's achroodextrin, $(C_{12}H_{20}O_{10})_2 + H_2O$, which is theoretically possible but has not yet been prepared. The author is engaged on the purification and examination of an achroodextrin of lower rotatory power and higher reducing properties, obtained by the action of diastase on starch. E. W. W.

Electrolytic Conversion of Nitriles into Amines. By FELIX B. AHRENS (*Zeit. Elektrochem.*, 1896, **3**, 99).—The author finds that nitriles are reduced to amines when solutions of them, which may be acid or alkaline, are placed in the cathode compartment of an electrolytic cell; hydrolysis of the nitrile takes place simultaneously, diminishing the yield of amine obtained, this being especially the case with alkaline solutions. Acetonitrile dissolved in 5 per cent. sulphuric acid gave ammonia alone, whilst with 3 per cent. acid, some ethylamine was obtained; propionitrile, in acid solution, gave considerable quantities of normal propylamine, whilst benzonitrile gave only benzylamine. Phenylethylamine was also obtained from benzylic cyanide. Alkaline solutions gave less favourable results. T. E.

Dibromodiethylamine. By SIEGMUND GABRIEL and GEORG ESCHENBACH (*Ber.*, 1897, **30**, 809—813).—Diphenoxydiethylamine, $NH(C_2H_4 \cdot OPh)_2$ (Weddige, Abstr., 1881, 1136), readily reacts with hydrobromic acid at 150° forming *dibromodiethylamine hydrobromide*, $NH(C_2H_4Br)_2,HBr$, which crystallises in colourless scales, and melts at 199—200°. The *picrate* melts at 128°, and the *bismuthoiodide* at 164—165°, whilst the *platinochloride* melts and decomposes at 222°. The bromine atoms cannot readily be removed by the action of aqueous potash, but when the hydrobromide is digested with aqueous silver nitrate, it is converted into *dihydroxydiethylamine nitrate*,

$$NH(C_2H_4 \cdot OH)_2,HNO_3,$$

which crystallises in colourless, pointed rhombs and melts at 69°. The *aurochloride* melts at 119—120°, and the platinochloride, which was first prepared by Wurtz (*Annalen*, 1862, **121**, 227), melts and decomposes at 160—161°. A. H.

Amidoethylic Alcohol (1 : 2-Ethanolamine). By LUDWIG KNORR (*Ber.*, 1897, **30**, 909—915).—Amidoethylic alcohol, or hydroxyethylamine, is best prepared by the action of ammonia on ethylenic oxide (Wurtz), dihydroxydiethylamine and trihydroxytriethylamine being also produced, in relative quantities which depend on the concentration of the ammonia employed. The three bases can then be separated without difficulty by fractional distillation. The same bases are formed by the action of ammonia on ethylene chlorohydrin, but they cannot be so easily isolated. Hydroxyethylamine is a thick, colourless oil with a faint odour resembling that of ethylenediamine. It boils at 171°, has a sp. gr. = 1·022 at 20°, the molecular refraction 16·17, and the molecular dispersion 0·50. It dissolves in about 100 parts of ether, and is more readily volatile with ether vapour than with steam. The base fumes in the air, and its vapour destroys cork, whilst its solution in water, with which it is miscible in all proportions, acts on the skin like a strong alkali. The *aurochloride* crystallises in long needles melting at about 190°. It forms a very

characteristic salt with 1′-paranitrophenyl-3′-methyl-4′-nitro-5′-pyrazolone, which the author proposes to term *picrolonic acid*. *Hydroxyethylamine picrolonate*, $C_2H_7NO,C_{10}H_8N_4O_5$, is sparingly soluble in water and alcohol, and crystallises in fascicular groups of yellow needles, which melt and decompose at about 225° when rapidly heated, at about 220° when slowly heated. The *dibenzoyl* derivative crystallises in thin plates melting at 76°. A. H.

Diethanolamine [Dihydroxydiethylamine]. By Ludwig Knorr (*Ber.*, 1897, **30**, 915—918. Compare the foregoing abstract).—*Dihydroxydiethylamine*, $NH(CH_2 \cdot CH_2 \cdot OH)_2$, crystallises in fibrous masses melting at 28°; it boils at 270° (pressure = 748 mm.) and at 217—218° (pressure = 150 mm.), has a sp. gr. = 1·0966 at 20°, the molecular refraction 27·08, and the molecular dispersion 0·880. It is hygroscopic, and resembles monhydroxyethylamine in its other properties, but is not volatile with steam. The *aurochloride* crystallises in long needles melting at about 122°; the readily soluble *picrate* melts at 109—110°, the *picrolonate* at about 216°. The *tribenzoyl* derivative could not be obtained in the crystalline state.

When the free base is heated at 160° with 70 per cent. sulphuric acid, it is converted into morpholine, which can thus be obtained in a purer condition than by any other method. A. H.

Triethanolamine [Trihydroxytriethylamine]. By Ludwig Knorr (*Ber.*, 1897, **30**, 918—921. Compare the two foregoing abstracts).—Trihydroxytriethylamine, $N(CH_2 \cdot CH_2 \cdot OH)_3$, was prepared in the free state by Wurtz. It boils at 277—279° (pressure = 150 mm.), has sp. gr. = 1·1242 at 20°, the molecular refraction 37·75, and the molecular dispersion 1·274. When caustic potash is added to its aqueous solution, a potassium salt separates in slender needles. The hydrochloride, which melts at 177°, is only sparingly soluble in water, and is insoluble in cold alcohol. The *platinochloride* melts at 118—119°, the *aurochloride* crystallises in four-sided plates containing $1H_2O$, and melts, after being dried, at 77—78°. The *picrate* melts at 126—127°, and is only sparingly soluble in alcohol and water. The *tribenzoate* is a viscid syrup. A. H.

Action of Free Bases on Salts. By Albert Colson (*Compt. rend.*, 1897, **124**, 502—504).—When di-isobutylamine hydrochloride is brought in contact with dry ammonia gas, the latter is rapidly absorbed. The dissociation pressure is 40 mm. at 0°, 53 mm. at 11°, and 85 mm. at 35°. On the other hand, ammonia gas has no action on piperidine hydrochloride, even under a pressure of 775 mm., but piperidine decomposes ammonium chloride, the dissociation pressure exceeding 1 atmosphere at the ordinary temperature, whilst at 0° it is 759—762 mm.

The decomposition of either hydrochloride by ammonia develops heat, and this development is a condition necessary to the results described. Direct experiment shows that, in both cases, there is actual displacement of the base. The decomposition of ammonium salts by the bases is a phenomenon of heterogeneous dissociation, comparable with the action of sulphuric acid on lead chloride (this vol., ii, 211).

Di-isobutylamine and piperidine form no basic hydrochlorides, but when their hydrochlorides are brought in contact with hydrogen chloride, the latter is immediately absorbed, and the dissociation pressures of the compounds formed depend only on the temperature. With di-isobutylamine hydrochloride, this pressure is 195 mm. at 0°, 253 mm. at 7·3°, and 760 mm. at 34°; with piperidine hydrochloride it is 355 mm. at 0°, and 462 mm. at 7·3°. C. H. B.

Preparation of Higher Amines of the Fatty Series: Pentadecylamine. By ELIZABETH JEFFREYS (*Ber.*, 1897, **30**, 898—901).—Hofmann's method for the preparation of fatty amines, does not apply to those high in the series, the yield apparently decreasing as the series advances; by slightly modified methods, such as starting with the acid bromamide, the middle members, for instance, octylamine, have been synthesized in yields of about 45 per cent., and since Lengfeld and Stieglitz have lately shown that acid bromamides in methylic alcohol solution undergo the Beckmann rearrangement with sodium methoxide, forming the urethane derivative of the amine, it seemed interesting to ascertain whether this method could be employed as a means of preparing the higher fatty amines; such was, in fact, found to be the case.

The *chloramide of palmitic acid*, $C_{15}H_{31}\cdot CO\cdot NHCl$, a compound melting at 70—71°, passes almost quantitatively, on treatment with sodium methoxide in methylic alcohol solution, into *pentadecylmethylurethane* (methylic *n*-pentadecylcarbamate), $C_{15}H_{31}\cdot NH\cdot COOMe$, a vitreous, crystalline mass melting at 61—62°; this compound, on hydrolysis with concentrated hydrochloric acid, or distillation with lime, yields *pentadecylamine*, $C_{15}H_{31}NH_2$, a colourless, crystalline substance melting at 36·5° and boiling at 298—301° (uncorr.), the yield of the amine being about 90 per cent. of the theoretical. It was subsequently found that the acid amide itself readily yielded the urethane derivative on treatment with sodium methoxide. It is, therefore, unnecessary to prepare the chloramide. *Pentadecylamine hydrochloride* forms a white, vitreous mass scarcely soluble in water, and yields a *platinochloride*, $(C_{15}H_{31}NH_2)_2,H_2PtCl_6$.

Pentadecylcarbamide, $C_{13}H_{31}\cdot NH\cdot CO\cdot NH_2$, is formed by the action of potassium cyanate on the hydrochloride; it melts at 109°. *Benzoylpentadecylamine* melts at 78°. J. F. T.

Action of Trimethylamine and Pyridine on Chlorhydrins. By HILDERICH HARTMANN (*Chem. Centr.*, 1896, i, 999—1000; from *Diss. Marburg*, 1896, 1—56).—According to V. Meyer and to Scholten, trimethyldihydroxypropylammonium chloride is formed by the action of trimethylamine on α-monochlorhydrin; its platinochloride melts at 230° (Scholten 220°), and its aurochloride at 155° (Scholten 190°). Unlike Scholten, the author finds that acetic chloride reacts only incompletely with the ammonium chloride at 160°, but by heating with acetic anhydride and sodium acetate, the *diacetoxypropyl* derivative is produced; this gives a *platinochloride* melting at 235—236°. Similarly, with benzoic chloride the action is incomplete, but benzoic anhydride at 150—160° forms the analogous *dibenzoyl* derivative; the *platinochloride* melts at 191°. By the action of hydriodic acid

at 100° on trimethyldihydroxypropylammonium chloride, the author has obtained two compounds, $C_3H_5I_2\cdot NMe_3I$, which Scholten obtained only at a higher temperature, and $CH_2I\cdot CH(OH)\cdot CH_2\cdot NMe_3Cl$. The latter forms an *aurochloride* melting at 101°, and a *platinochloride* which blackens at 176° and decomposes completely at 194°. By the action of nitric acid on trimethyldihydroxypropylammonium platinochloride, trimethylamine and a new compound, whose analysis shows a composition nearer that of homohydroxybetaine than of homohydroxymuscarine are formed. With platinic chloride, this substance gives a compound, $[COOH\cdot CH(OH)\cdot CH_2\cdot NMe_3]_2PtCl_6$, melting at 233°, and with gold chloride a compound melting at 168—172°. Both salts were analysed. The fact that a copper salt may also be formed indicates the presence of a carboxyl group. In accordance with Niemilovicz's observation, but not with Scholten's, two products are obtained by the action of trimethylamine on α-dichlorhydrin, namely, hexamethylhydroxypropylenediammonium chloride, the platinochloride of which melts at 266° and the aurochloride decomposes at 246°, and trimethylchlorhydroxypropylammonium chloride which gives a platinochloride melting at 168° and an aurochloride melting at 163°. The latter compound is identical with that of the same name obtained by Partheil (Abstr., 1892, 950) in a different way. Its constitution

$$CH_2Cl\cdot CH(OH)\cdot CH_2\cdot NMe_3Cl$$

is proved by the above synthesis.

By the action of trimethylamine on β-dibromhydrin, an epibromhydrin is first formed,

$$CH_2OH\cdot CHBr\cdot CH_2Br + NMe_3 = O<\begin{matrix}CH_2\\ | \\ CH\cdot CH_2Br\end{matrix} + NMe_3HBr,$$

$$O<\begin{matrix}CH_2\\ | \\ CH\cdot CH_2Br\end{matrix} + 2NMe_3 + H_2O = OH\cdot CH(CH_2\cdot NMe_3\cdot OH)_2$$

These intermediate products were not isolated, but hexamethylhydroxypropylenediammonium chloride was obtained by means of silver chloride and hydrochloric acid. Trimethylamine acts on β-dichlorhydrin in a manner analogous to the above.

By the action of trimethylamine on allylic tribromide, the author, like Scholten, only obtained a trimethylbromallylammonium chloride, which is identical with the compound obtained by Partheil (*loc. cit.*).

By the action of trimethylamine on epichlorhydrin, hexamethylhydroxypropylenediammonium chloride was obtained, as Scholten found, and from the mother liquor the epi-compound identical with Partheil's anhydrobromoisomuscarine.

By the action of pyridine on β-dichlorhydrin, an additive product appears to be formed which easily decomposes.

Pyridine reacts with epichlorhydrin to form two compounds, the aurochlorides of which, (I) and (II), melt respectively at 235° and 146°.

I. $AuCl_3\cdot C_5H_5\cdot NCl\cdot CH_2\cdot CHOH\cdot CH_2\cdot N(CCl)\cdot C_5H_5\cdot AuCl_3$.

II. $AuCl_3\cdot CH_2Cl\cdot CHOH\cdot CH_2\cdot N(CO)\cdot C_5H_5$. E. W. W.

Condensation of Acetone on Boiling with Excess of Zinc Chloride. By P. N. Raikow (*Ber.*, 1897, **30**, 905—906).—On boiling acetone with excess of zinc chloride for many hours, an oily layer gradually separates, becoming thicker as the boiling is prolonged. The

product, which evidently contained many substances, was fractionated, and the fractions boiling at 161—162° and 251—252° analysed; the numbers obtained corresponded better with those for terpene than those for mesitylene. J. F. T.

Conversion of Ketones into α-Diketones. II. By MICHELE FILETI and GIACOMO PONZIO (*J. pr. Chem.*, 1897, [ii], **55**, 186—201. Compare Abstr., 1895, i, **15**, 499).—The authors have extended their investigations on the oxidation of ketones by nitric acid to ketones of the type $R\cdot CH_2\cdot CO\cdot CH_2R'$. Diethyl and dipropyl ketones, as might be expected from their symmetrical structure ($R = R'$), yield only one diketone each, $R\cdot CO\cdot CO\cdot CH_2R$, and one dinitrohydrocarbon, $R\cdot CH(NO_2)_2$. Ethyl isopropyl ketone yields only one diketone, in harmony with the fact that it contains only one CH_2 group adjoining the CO group; further, it yields only one dinitrohydrocarbon, dinitroethane. Ethyl propyl ketone yields the two possible diketones, $R\cdot CO\cdot CO\cdot CH_2\cdot R'$ and $R\cdot CH_2\cdot CO\cdot CO\cdot R'$, and the two possible dinitroethanes, $R\cdot CH(NO_2)_2$ and $(NO_2)_2CH\cdot R'$. From ethyl isobutyl ketone, only the diketone $CH_3\cdot CO\cdot CO\cdot CH_2Pr^{\beta}$ could be identified with certainty, and only dinitroethane. It may thus be asserted that the dinitro-derivative obtained is always derived from the alcohol radicle to which belongs the methylene group that is converted into carbonyl. Lastly, among the products obtained from ethyl isopropyl and ethyl isobutyl ketones were substances of the type $CH_3\cdot C(NO_2)_2\cdot CO\cdot R'$; these are unstable, being hydrolysed slowly by dilute acids and water, more quickly by alkalis, into dinitroethane, $CH_3\cdot CH(NO_2)_2$, and acids, $OH\cdot CO\cdot R'$. Palmitone yields neither diketone nor dinitrohydrocarbon.

Propionylbutyryl, $COEt\cdot COPr^{\alpha}$, from dipropylketone, is an oil, lighter than water, and sparingly soluble in it; the *dioxime* melts at 167—168°, the *osazone* at 106°. *Dipropionyl*, $COPr^{\alpha}\cdot COPr^{\alpha}$, from ethyl propyl ketone, was only obtained mixed with acetylbutyryl; its *osazone* melts at 160—161°, the impure *dioxime* at 156—159°. *Isobutyryldinitroethane*, $CH_3\cdot C(N_2O_4)\cdot COPr^{\beta}$, from ethyl isopropyl ketone, melts at 58°; *isovaleryldinitroethane*, $CH_3\cdot C(N_2O_4)\cdot CO\cdot CH_2Pr^{\beta}$, from ethyl isobutyl ketone, is also crystalline; both have an odour resembling that of camphor. C. F. B.

Electrolysis of Salts of Organic Acids. By J. F. CARL SCHALL (*Zeit. Elektrochem.*, 1896, **3**, 83).—Dithiocarboxylic acids, or their salts with the alkali metals, are decomposed by electrolysis of their aqueous solutions according to the equation $2R\cdot CSSM = 2R\cdot CSS + 2M$; and $2RCSS = (RCS)S - S(SCR)$. The author thinks it probable that the carboxylic acids decompose primarily in the same way, the peroxide thus formed subsequently decomposing into the corresponding anhydride and oxygen or into carbonic anhydride and the corresponding hydrocarbon. T. E.

Action of Bromine and Hydrogen Bromide on Ethylic Acetate. By BOLESLAS EPSTEIN (*Compt. rend.*, 1897, **124**, 688—689). —When ethylic acetate and bromine, in molecular proportion, are

heated together in sealed tubes, there is, contrary to the statement of Crafts (*Compt. rend.*, 1863, **56**, 707) a considerable formation of hydrogen bromide, the other products being ethylic bromide and monobromacetic acid without any appreciable quantity of ethylic monobromacetate. Ethylic α-monobromopropionate under the same conditions at 180—200°, yields a considerable quantity of hydrogen bromide, together with ethylic bromide, ethylic dibromopropionate, and dibromopropionic acid, the proportion of the dibromopropionate increasing considerably with the time of heating.

It would seem that the products result from two successive reactions, $CMeHBr\cdot COOEt + Br_2 = CMeBr_2\cdot COOEt + HBr$ and $CMeBr_2\cdot COOEt + HBr = EtBr + CMeBr_2\cdot COOH$, the latter being reversible and the rate of change being different in the two directions. C. H. B.

Fatty Substances found in Egyptian Tombs at Abydos. By Charles Friedel (*Compt. rend.*, 1897, **124**, 648—653).—The substances described in this paper were found in earthen vases in the interior of Egyptian tombs which are believed to be earlier than the first dynasty. They were no doubt intended as provision for the dead; the specimens examined included.

(1) Several kilos. of a pale brown, porous, granular substance, covered with a black outer layer. It consists of palmitic acid mixed with less than 51 per cent. of palmitin, and there can be little doubt that the original substance was palm oil, which, in course of time, has been gradually oxidised, and partially saponified owing to the readier oxidation of the glycerol. Some acids of the succinic series (? azelaic and pimelic) are also present. The outer black layer seems to be the oxidation product of some resinous substance, used probably to protect the palm oil.

(2) A firmer, more granular, paler mass, consisting of stearic acid, with about 30 per cent. of stearin, the original substance being in all probability beef or mutton fat.

(3) A dark brown, granular cake, consisting of palmitic acid, with 41 per cent. of palmitin.

(4) A pale yellow-brown, light, porous mass, which gives off but little odour when it burns, and leaves a considerable quantity (about 46 per cent.) of ash of the composition SO_2, 13·67; CaO, 31·42; Al_2O_3 and Fe_2O_3, 9·34; K_2O, 15·04; Na_2O, 1·33. It contains grape seeds and also some seeds which seemed to be a cereal, and there is little doubt that the original substance was a cake made of raisins and some cereal.

Some small vases were found to contain powdered galena mixed with some fatty matter, doubtless for use as a cosmetic. C. H. B.

Formulæ of Cerotic and Melissic Acids. By Theod. Marie (*Bull. Soc. Chim.*, 1896, [iii], **15**, 565—569).—The author has endeavoured to fix more definitely the formulæ of cerotic and melissic acids obtained from bees-wax. The analysis of the free acids, of their ethereal salts, and of numerous derivatives point to the identity of melissic acid obtained from carnaúba wax with that obtained from bees-wax. The formula $C_{30}H_{60}O_2$, generally accepted for the former acid, must therefore be assigned to the latter. The free melissic acid

extracted from bees-wax is also identical with that obtained by the action of soda-lime on myricylic alcohol. In the case of cerotic acid, the numbers obtained in the analysis of the acid itself, its ethereal salts, the salts of barium and silver, and eight of its derivatives indicate that this acid must be represented either by the formula $C_{25}H_{50}O_2$ or $C_{26}H_{52}O_2$, the former being the more probable. In any case, Brodie's formula, $C_{27}H_{54}O_2$, must be rejected. By the action of concentrated hydriodic acid and red phosphorus on the acid at 210—240°, a hydrocarbon was obtained readily soluble in ether and benzene, insoluble in alcohol, and melting at 54°. Its formula is either $C_{25}H_{52}$ or $C_{26}H_{54}$. In the former case, it would be placed between the hydrocarbons tetracosane (m. p. 51·1°) and heptacosane (m. p. 59·5°) prepared by Krafft. In addition to this hydrocarbon, an acid is also formed in the above reaction melting at 95°, and therefore considerably above cerotic acid itself (77·5°). This is in accordance with Krafft's observations on the action of hydriodic acid on the lower fatty acids. It appears almost certain that $C_{25}H_{50}O_2$ represents the composition of cerotic acid and that it therefore follows lignoceric acid in the series. A. C. C.

Bromo-derivatives of Cerotic and Melissic Acids. By THEOD. MARIE (*Bull. Soc. Chim.*, 1896, [iii], 15, 569—575).—*Bromocerotic acid*, $C_{24}H_{48}Br\cdot COOH$, is obtained by acting on cerotic acid with the theoretical quantity of bromine in the presence of red phosphorus, the mixture being at first kept cool and finally heated at 100° until the evolution of hydrogen bromide ceases. It is very soluble in benzene, from which it crystallises on evaporation in mammilated masses consisting of fine needles melting at 66·5°. It is very stable, but when heated to 220—250° undergoes decomposition with disengagement of gas. *Ethylic bromocerotate*, $C_{24}H_{48}Br\cdot COOEt$, is obtained when a solution of the above acid in 95 per cent. ethylic alcohol is boiled for 3 hours with the addition of sulphuric acid. It is more soluble in alcohol than either cerotic acid or its bromo-derivative, and crystallises from this solvent in felted masses of fine needles melting at 46·5°.

Dibromocerotic acid, $C_{24}H_{47}Br_2\cdot COOH$, is prepared by the action of excess of bromine on the monobromo-derivative in presence of red phosphorus. The product of the reaction is dissolved in hot benzene, from which, on cooling, crystals of the monobromo-derivative are first obtained; the mother liquors, on concentration, yield a crystalline mass of the dibromo-derivative melting at about 30°.

Bromomelissic acid, $C_{29}H_{58}Br\cdot COOH$, is obtained in a similar manner to the corresponding cerotic acid derivativte; it crystallises from hot benzene in small masses consisting of radiating needles melting at 79·5°. The *ethylic* salt of this acid, prepared similarly to the corresponding cerotate, crystallises from boiling alcohol in fine, long needles melting at 65°. *Dibromomelissic acid*, $C_{29}H_{57}Br_2\cdot COOH$, is obtained in a similar manner to dibromocerotic acid. The benzene solution of the products of the action yields first the monobromo-derivative and then, on complete evaporation of the solvent, a yellowish residue melting at 47°, and consisting almost entirely of the dibromo-acid. In this experiment, the displacement of the second hydrogen atom takes place with much greater difficulty than the first. Hitherto,

the dibromo-derivatives of the higher fatty acids have only been obtained by the addition of bromine to the corresponding unsaturated acids. A. C. C.

Comparison of the Derivatives of Cerotic and Melissic Acids with those of the Fatty Acids. By THEOD. MARIE (*Bull. Soc. Chim.*, 1896, [iii], 15, 590—591).—A study of the chemical and physical properties of the derivatives of cerotic and melissic acids shows that these acids have a precisely similar constitution to palmitic and stearic acids, and that they are, in fact, true fatty acids. It is pointed out that the same methods of preparation are applicable in both cases, and that the melting points and solubilities are in direct relation with their increased molecular weights. A table is given in which the melting points of 15 derivatives of cerotic and melissic acids are compared with those of the corresponding derivatives of myristic, palmitic, and stearic acids. A. C. C.

Decomposition of Ethoxalic Chloride [Ethylic Chloroglyoxylate] with Elimination of Carbonic Oxide. By GIUSEPPE GRASSI-CRISTALDI (*Gazzetta*, 1897, 27, i, 27—34).—W. Wislicenus has shown (Abstr., 1894, i, 323) that derivatives of ethylic oxalacetate decompose when heated, liberating carbonic oxide, and the author finds that, on passing the vapour of ethylic chloroglyoxylate (Anschütz, Abstr., 1886, 1011) through a glass tube heated at 200°, and cooling the product in a freezing mixture, ethylic chlorocarbonate is produced, in accordance with the equation $COCl\cdot COOEt = CO + Cl\cdot COOEt$.

When the vapour of ethylic oxalate is passed through a glass tube at a low red heat, it decomposes in accordance with the equation: $COOEt\cdot COOEt = CO_2 + C_2H_4 + H\cdot COOEt$; no carbonic oxide is produced, but a little formic acid is obtained owing to secondary action.

W. J. P.

Hydroxy- and Amido-derivatives of Cerotic and Melissic Acids. By THEOD. MARIE (*Bull. Soc. Chim.*, 1896, [iii], 15, 576—583). —*Hydroxycerotic acid*, $OH\cdot C_{24}H_{48}\cdot COOH$, is obtained by the action of caustic soda on the monobromo-derivative in alcoholic solution. When crystallised, first from light petroleum and then from alcohol, in which it is very soluble, it forms tufts of fine radiating needles melting at 86·5°. From benzene, it crystallises in microscopic needles. It may also be prepared by the action of lead acetate on ethylic bromocerotate. *Ethylic acetoxycerotate*, which is first formed, crystallises from ether in colourless needles melting at 57—58°. This compound on saponification with caustic potash in alcoholic solution yields the hydroxy-acid. The salts of barium and magnesium are obtained as white, flocculent precipitates on mixing alcoholic solutions of the acid and of the metallic acetates. When heated at 170—200°, 2 molecules of hydroxycerotic acid lose 1 molecule of water, yielding a colourless substance, which does not unite with bromine, is soluble in ether and benzene, and melts at 76—77°. This anhydride, when heated with a dilute aqueous solution of caustic potash, undergoes conversion into the original acid.

Amidocerotic acid, $NH_2\cdot C_{24}H_{48}\cdot COOH$, is prepared by the action of

ammonia on bromocerotic acid in alcoholic solution, and forms small, rounded masses of radiating needles. After heating on the water bath, and washing consecutively with water, alcohol, and boiling ether, a white, powdery crystalline residue remains, melting at 215°. It is practically insoluble in alcohol, ether, benzene, ethylic acetate, amylic alcohol, and chloroform, but dissolves in an alcoholic solution of potash and in boiling glacial acetic acid.

Hydroxymelissic acid, $OH\cdot C_{29}H_{58}\cdot COOH$, is prepared by acting on the bromo-acid with alcoholic potash. It crystallises in masses of microscopic needles, which, after three crystallisations from hot benzene, followed by two crystallisations from ether, melt at 96·5°. When heated at 190—200°, this acid undergoes an analogous decomposition to hydroxycerotic acid.

Amidomelissic acid, $NH_2\cdot C_{29}H_{58}\cdot COOH$, is prepared in a similar manner to the cerotic acid derivative. When thoroughly washed with boiling water, boiling alcohol, and ether, it forms a white powder, melting with decomposition at 205°; it dissolves in aqueous and alcoholic solutions of caustic potash and in boiling glacial acetic acid, but is insoluble in almost all the ordinary organic solvents. In the preparation of these amido-derivatives, small quantities of the hydroxy-acids are also formed. A. C. C.

Derivatives of Methylic Monobromodimethylacetoacetate. By MAX CONRAD (*Ber.*, 1897, **30**, 856—863. Compare Abstr., 1896, i, 409).—[With ANTON KREICHGAUER.]—*Methylic γ-bromodimethylacetoacetate* is readily obtained as a yellowish oil when the requisite quantity of bromine is added in the cold to methylic dimethylacetoacetate; as this oil decomposes on distillation, it is necessary to use it in the crude form.

Methylic methoxydimethylacetoacetate, $OMe\cdot CH_2\cdot CO\cdot CMe_2\cdot COOMe$, can be prepared by treating the monobromomethylic salt with sodium methoxide; after being washed with light petroleum and recrystallised from ether, it is obtained in hard, glistening crystals melting at 70° and distilling at 240—242°.

Methylic acetoxydimethylacetoacetate, $OAc\cdot CH_2\cdot CO\cdot CMe_2\cdot COOMe$, is a colourless oil which distils at 244—246°; its sp. gr. is 1·135 at 16°/15°.

Dihydroxydimethylacetoacetic acid lactone, $O<\begin{matrix}CH(OH)\cdot CO\\ | \\ CO\text{———}CMe_2\end{matrix}$, is obtained when either the methylic salt or the acetate described above is brominated in carbon bisulphide solution and then left in contact with water for several weeks. It is best purified by washing with ether; it crystallises in prisms which melt at 168—169°, at the same time evolving carbonic anhydride and yielding a white sublimate. The *acetate* of the lactone, $O<\begin{matrix}CH(OAc)\cdot CO\\ | \\ CO\text{———}CMe_2\end{matrix}$, exists in two isomeric forms, one of which melts at 114° and the other at 154°. These two compounds are being further investigated.

When this lactone is shaken with soda solution at the ordinary temperature, it is gradually dissolved, and the addition of hydrochloric acid to this solution yields, in the course of a day or two, the isomeric 2-*dimethyl*-3:4-*butanonaloic acid*, $COH\cdot CO\cdot CMe_2\cdot COOH$, melting at 138°.

The same acid can be obtained by dissolving the lactone in boiling ethylic alcohol and then precipitating with water.

[With RUPPERT.]—*β-Dimethylmalic acid*,

$$COOH\cdot CH(OH)\cdot CMe_2\cdot COOH,$$

is formed when an alcoholic solution of the lactone or of the isomeric acid is added to sodium hydroxide solution at 0°; the mixture is kept for 12 hours, and then evaporated on the water bath. The acid crystallises from boiling ethylic acetate in prisms, and melts at 129°. Its solution yields precipitates with ferric chloride and silver nitrate, but not with lead acetate, zinc sulphate, or copper sulphate.

Isobutyrylformaldehyde, 3-methyl-2-butanonal, $CHMe_2\cdot CO\cdot COH$, is the product formed when the lactone or its isomeride is boiled with water. It crystallises in prisms, melts at 95°, has a sweet taste, and is readily soluble in ether and alcohol. Its *osazone*,

$$CHMe_2\cdot C(:N_2HPh)\cdot CH:N_2HPh,$$

melts at 115°, and its *dioxime* at 110°.

When isobutyrylformaldehyde is treated with a dilute alcoholic solution of soda, it yields α-hydroxyisovaleric acid, melting at 83°.

Methylic acetoxymethoxydimethylacetoacetate,

$$OAc\cdot CH(OMe)\cdot CO\cdot CMe_2\cdot COOMe,$$

melts at 54° and distils at 220—240°, undergoing partial decomposition.

J. J. S.

Transformations of Sugars: Levulinic Acid. By MARCELLIN P. E. BERTHELOT and GUSTAVE ANDRÉ (*Compt. rend.*, 1897, **124**, 645—648). —*Levulinic Acid.*—Heat of combustion (1 gram) at constant volume 4975·2 cal., molecular heat of combustion + 577·1 Cal. at constant volume and + 577·4 Cal. at constant pressure; heat of formation from its elements, solid acid, + 170·1 Cal., liquid acid + 167·9 Cal., dissolved acid + 166·5 Cal.

Levulinic lactone or olide (liquid).—Heat of combustion (1 gram) 6112·0 cal., molecular heat of combustion + 599·2 Cal. at constant volume and + 599·5 Cal. at constant pressure; heat of formation from its elements + 79·0 Cal.; heat of hydration (liquid anhydride, liquid water, and liquid acid) + 19·9 Cal., which is higher than the corresponding value for most organic anhydrides.

The formation of levulinic acid from glucose, $C_6H_{12}O_6$ diss. + $C_5H_8O_3$ diss. + $H\cdot COOH$ diss. + H_2O, should therefore develop + 36·7 Cal. The conversion of dissolved glucose into dissolved alcohol and gaseous carbonic anhydride develops + 33·0 Cal., and its conversion into dissolved lactic acid develops + 34 Cal. It is evident, therefore, that all three transformations of glucose are exothermic, and they develop practically the same quantities of heat. The conversion of glucose into acetic acid, if possible, would develop + 51·8 Cal., and the synthesis of glucose from formaldehyde would develop + 57·6 Cal., if + 40·4 Cal. be accepted as the heat of formation of dissolved formaldehyde. The conversion of glucose into formaldehyde would, on the other hand, absorb − 57·6 Cal.

Glucose behaves as a particularly mobile molecule, and this is doubtless due to its formation from aldehydic groups, the hydrogen and oxygen atoms oscillating between several carbon centres. The authors suggest that in the production of alcohol it is not the living

cell itself but some compound secreted by it that brings about the transformation of the glucose. C. H. B.

Synthesis of δ-Dimethyl-levulinic Acid. By MAX CONRAD (*Ber.*, 1897, **30**, 864—865).—Few attempts seem to have been made to condense the γ-bromo-derivatives of ethylic dialkylacetoacetates with the sodium compound of ethylic malonate, although by this means many compounds could be synthetically prepared the formation of which by other methods would be long and tedious.

Ethylic bromodimethylacetoacetate reacts readily with methylic sodiomalonate, and although the yield is somewhat decreased by the formation of methylic ethanetetracarboxylate, yet a moderately large quantity of the condensation product, *methylic* 1-*dimethyl*-2-*keto*-4-*carboxyadipate*, $(COOMe)_2 \cdot CH \cdot CH_2 \cdot CO \cdot CMe_2 \cdot COOMe$ [*ketoisohexane-ααδ-tricarboxylate*], is obtained as a thick oil boiling at 300—320° with partial decomposition.

On hydrolysing the methylic salt with dilute sulphuric acid, 2 molecules of carbonic anhydride are eliminated, and *δ-dimethyl-levulinic acid*, $COOH \cdot CH_2 \cdot CH_2 \cdot CO \cdot CHMe_2$, is formed. This acid crystallises from warm, light petroleum in long, colourless needles melting at 40—41°, and is identical with the acid obtained by Fittig from isoheptenic acid. J. F. T.

Action of Potassium Cyanide on 1 : 4-Olides [Lactones]. By EDMOND BLAISE (*Compt. rend.*, 1897, **124**, 89—91).—When isocaprolactone is heated in a sealed tube for 5 hours at 270—280° with potassium cyanide and the product treated with acetic chloride, an acid anhydride melting at 240—250° is obtained. This reacts with aniline, forming the compound $COOH \cdot CHPr^{\beta} \cdot CO \cdot NHPh$, which crystallises from benzene in nacreous plates melting at 142—144°, and on boiling with dilute hydrochloric acid yields isopropylsuccinic acid melting at 118°. When the above aniline derivative is kept for some minutes at its boiling point, it undergoes conversion into the compound $\left.\begin{matrix} CHPr^{\beta} \cdot CO \\ | \\ CH_2 - - CO \end{matrix}\right\rangle NPh$, which crystallises from dilute alcohol in needles melting at 95—96°. Had the action of potassium cyanide on the above lactone been analogous to the reactions occurring in the cases studied by Wislicenus (Abstr., 1886, 879), the acid $COOH \cdot CMe_2 \cdot CH_2 \cdot CH_2 \cdot COOH$ would have been formed instead of isopropylsuccinic acid. A. C. C.

Cyanide and a Dibasic Acid and its Amide derived from Cerotic Acid. By THEOD. MARIE (*Bull. Soc. Chim.*, 1896 [iii], **15**, 583—590).—*Cyanocerotic acid*, $CN \cdot C_{24}H_{48} \cdot COOH$, is prepared by the action of potassium cyanide on ethylic bromocerotate in alcoholic solution. On treating the aqueous solution of the potassium salt of this acid with dilute sulphuric acid, the acid separates as a transparent precipitate which becomes opaque on boiling. From benzene, it is obtained in rounded masses, consisting of fine needles melting constantly at 86°, whilst from ether it melts at 88°. When heated at 180—190°, it undergoes partial decomposition into carbonic anhydrile and cerotonitrile, $C_{24}H_{49} \cdot CN$, melting at 58—59°, and identical with the product of the dehydration of cerotamide (this vol., i, 266).

The *amic acid*, $NH_2 \cdot CO \cdot C_{24}H_{48} \cdot COOH$, is obtained when the preceding acid is boiled for 12 hours with caustic potash in alcoholic solution. When separated from its potassium salt by the addition of a dilute mineral acid, it is obtained as a granular precipitate by pouring its alcoholic solution into ether. From hot benzene, it crystallises in bundles of fine needles, radiating from a point. When heated to 160°, it undergoes decomposition, carbonic anhydride being evolved and cerotamide, melting at 109—110°, formed. The decomposition is, however, not complete, the residue always containing some of the unaltered acid. By the prolonged action of an alcoholic solution of caustic potash on the preceding acid, or on cyanocerotic acid itself, the *dibasic acid*, $C_{24}H_{48}(COOH)_2$, is obtained, together with hydroxycerotic and cerotic acids, from which it can only be separated with very great difficulty. By fractional precipitation with barium acetate, a barium salt was prepared containing very nearly the percentage of barium required for the salt of the dibasic acid; from this an acid was obtained melting at 112—114°. When heated to 150°, it readily decomposes into carbonic anhydride and cerotic acid. The author is of opinion that the bromine atom in monobromocerotic acid is in the α-position relative to the carboxyl group. A. C. C.

Optical Behaviour of Malic Acid. By CHR. WINTHER (*Chem. Centr.*, 1896, ii, 22—23; from *Nyt Tidsskrift Fysik Kemi*, 1896, 122—131).—After giving an account of the relation of malic acid and the malates to Oudemans' law, the author shows how Nasini's and Gennari's assumption of two active components may be explained on the asymmetrical constitution of malic acid by supposing two active ions to be formed in solution. Like all dicarboxylic acids, malic acid is first dissociated into a monocarboxylic acid. Walden's conversion of the one active variety into the other by means of phosphorus pentabromide is explained, the formulæ I and II being attributed to these compounds. On rotating II, the formula III is obtained, and the transformation is seen to consist merely in a change of position of the hydroxyl group.

$$
\begin{array}{ccc}
\begin{array}{c}
\mathrm{COOH} \\
| \\
\mathrm{H-C-OH} \\
| \\
\mathrm{H-C-H} \\
| \\
\mathrm{COOH}
\end{array}
&
\begin{array}{c}
\mathrm{COOH} \\
| \\
\mathrm{HO-C-H} \\
| \\
\mathrm{H-C-H} \\
| \\
\mathrm{COOH}
\end{array}
&
\begin{array}{c}
\mathrm{COOH} \\
| \\
\mathrm{H-C-H} \\
| \\
\mathrm{H-C-OH} \\
| \\
\mathrm{COOH}
\end{array}
\\
\text{I.} & \text{II.} & \text{III.}
\end{array}
$$

Water is first split off and then hydrogen bromide added. Now the two carboxyl groups are not of equal value, the one being influenced by the proximity of the hydroxyl group, and by assuming these groups to possess a strong intramolecular attraction, whilst in bromosuccinic acid the bromine has a repulsive action on the carboxyl group, then it follows that the bromine will not take the place of the hydroxyl group, and so the change is effected. On this hypothesis, all compounds of constitution analogous to malic acid should be capable of similar transformations; for instance, aspartic acid (by

removal of ammonia), ethoxysuccinic acid (by removal of alcohol), propylenediamine, &c. E. W. W.

Ketocarboxylic Acids: β-Acetylglutaric Acid. By WILLIAM O. EMERY (*Annalen*, 1897, **295**, 94—126).—*β-Acetylglutaric acid*,

$$COMe{\cdot}CH(CH_2{\cdot}COOH)_2,$$

is obtained by heating ethylic β-acetyltricarballylate with concentrated hydrochloric acid, and submitting the anhydride produced in this way to the action of water in sealed tubes; it crystallises in aggregates of deliquescent needles, and melts indefinitely at 47—50°. The ketodilactone, $C_7H_8O_4$, the initial product of the change (Abstr., 1891, 422), crystallises in long, lustrous needles, melts at 101—102°, and boils at 205° under a pressure of 12 mm.; it resists the action of sodium carbonate, and is only in part converted into β-acetylglutaric acid when crystallised from concentrated hydrochloric acid. The *dimethylic* salt of β-acetylglutaric acid boils at 144° under a pressure of 12 mm., and has a sp. gr. = 1·1441 at 20°/4°; the *diethylic* salt boils at 154° under a pressure of 11—12 mm., and has a sp. gr. = 1·0798 at 20°/4°. The *hydrogen methyl* salt crystallises in needles, and melts at 99°; distillation resolves the substance into methylic alcohol and the ketodilactone. When the dimethylic salt is mixed with phenylhydrazine, water is eliminated, and the compound $C_{15}H_{20}N_2O_4$ produced; it crystallises from dilute acetic acid in slender needles, and melts at 83°. The *sodium* and *hydrogen sodium* salts are crystalline, and the *hydrogen potassium* salt separates from the aqueous solution in slender needles, but the *potassium* salt is deliquescent and syrupy; the *barium* salt crystallises from water with $1H_2O$, and from alcohol with $3H_2O$. The *strontium* salt contains $2H_2O$, and the calcium salt is a syrup; the *magnesium* and *silver* salts are anhydrous, and the *copper* salt contains $1H_2O$.

Ammonium β-acetylglutaramate, $C_7H_{14}N_2O_4$, produced when the ketodilactone is treated with ammonia, crystallises from a mixture of ether and alcohol in white needles melting at 141—142°. The *ketolactoneimide* of β-acetylglutaric acid, $C_7H_9NO_3$, is obtained by adding sufficient 50 per cent. acetic acid to liberate ammonia from the ammonium salt of β-acetylglutaramate; it crystallises from methylic alcohol in highly refractive prisms, and melts at 144—145°. The monimide combines with phenylhydrazine at 130°, forming the *compound*

$$C_{13}H_{15}N_3O_2,$$

which crystallises from methylic alcohol in microscopic octahedra and melts at 228—229°.

The *ketodiimide* of β-acetylglutaric acid, $C_7H_{10}N_2O_2$, is obtained by heating ethylic β-acetylglutarate with alcoholic ammonia, and is also produced when ammonium β-acetylglutaramate is heated at 150—160° until water vapour ceases to be liberated, or when the monimide is heated at 150° in an atmosphere of ammonia; it crystallises from methylic alcohol, and melts above 275°, at which temperature it darkens. Acetic anhydride has no action on the ketodiimide at 100°, but in sealed tubes at 150—160° it is converted into an *acetyl* derivative, $C_9H_{12}N_2O_3$, which crystallises from benzene in snow-white plates and melts at 142—144°.

The *ketolactonanil*, $C_{13}H_{13}NO_3$, is obtained by the action of aniline en

the ketodilactone dissolved in absolute alcohol or chloroform; it crystallises from a mixture of ether and ethylic acetate in colourless leaflets, and melts at 154°. It dissolves in concentrated sulphuric acid without undergoing change, and is also soluble in ammonia, being deposited again on evaporation. The *ketoanilimide*, $C_{13}H_{14}N_2O_2$, produced when the foregoing substance is heated with alcoholic ammonia in sealed tubes at 100°, separates from alcohol in small, compact crystals, and melts at 207·5°. The *ketolactonorthotolil*, $C_{14}H_{15}NO_3$, crystallises from hot water in aggregates of small needles and melts at 138°; the *paratolil* crystallises from methylic alcohol in colourless leaflets and melts at 135°. The *ketoparatolilimide*, $C_{14}H_{16}N_2O_2$, is obtained from the paratolil and alcoholic ammonia, and crystallises from methylic alcohol in microscopic prisms melting at 189°. The *ketolacton-α-naphthil* and the *ketolacton-β-naphthil*, $C_{17}H_{15}NO_3$, melt at 153° and 186° respectively.

The *ketobisphenylhydrazide anhydride*, $C_{19}H_{20}N_4O_2$, obtained by heating the ketodilactone with phenylhydrazine (2 mols.), crystallises from dilute acetic acid in small needles melting at 222—223°; the *acetyl* derivative melts at 243°. The *ketolactonephenyl-α-ethylhydrazide anhydride*, $C_{15}H_{18}N_2O_3$, is produced on heating the ketodilactone with α-ethylphenylhydrazine (1 mol.) at 160°, and melts at 195°; both hydrazine compounds give a rose-coloured solution in concentrated sulphuric acid, which becomes dark red on the addition of ferric chloride.

Reduction of the ketodilactone with sodium amalgam gives rise to the lactonic *acid*, $C_7H_{10}O_4$, which crystallises in small needles, melts at 78—79°, and boils at 225° under a pressure of 20 mm.; the *silver* salt forms colourless, microscopic crystals.

Hydriodic acid converts the ketodilactone into β-ethylglutaric acid, which melts at 73° (compare Komnenos, *Annalen*, **218**, 167).

M. O. F.

Lyxonic Acid and Lyxitol.—By GABRIEL BERTRAND (*Bull. Soc. Chim.*, 1896, [iii], **15**, 592—594).—The author gives an account of the results he had obtained in the study of lyxonic acid and some of its derivatives at the time of the publication of a paper on the same subject by Fischer and Bromberg (Abstr., 1896, i, 348). For the separation of lyxonic acid from its stereoisomeride, xylonic acid, advantage is taken of the slight solubility of a compound of cadmium xylonate with cadmium bromide, the lyxonic acid being separated from the mother liquors.

The phenylhydrazide of lyxonic acid crystallises with $2H_2O$ (compare Abstr., 1896, i, 667) and melts at 142°, but when anhydrous at 148—149°. No crystalline phenylhydrazide of xylonic acid could be prepared. By the reduction of the lactone of lyxonic acid, lyxose was obtained, and this, on further reduction with sodium amalgam, yielded lyxitol as a nearly colourless syrup. No compound of lyxitol with benzaldehyde could be obtained.

Directions are given for the preparation of xylonic acid in quantity from molasses.

A. C. C.

Cryoscopic Determination of the Constitution of Amides. By ARTHUR LACHMANN (*Zeit. physikal. Chem.*, 1897, **22**, 170—172).—

Auwers has shown that hydroxy-compounds are, in general, cryoscopically abnormal, as also are very many acid amides (Abstr., 1894, ii, 133; 1895, ii, 41). As the amides are probably divisible into two classes, the true amides and the imido-compounds R·C(OH)·NH, it is possible that the abnormal behaviour is characteristic of the latter. Oxamethane has been shown by Wallach to contain no hydroxyl group, and the author therefore studied its cryoscopic behaviour, employing methylic oxalate as a solvent. The molecular weight obtained varied from 114 to 226, so that this compound also behaves abnormally, and the abnormality is not an indication of the hydroxylic nature of the amide. L. M. J.

Thiohydantoins. IV. By RUDOLF ANDREASCH (*Monatsh.*, 1897, **18**, 56—94. Compare Abstr., 1896, i, 89, &c.).—Citraconic acid, or its anhydride, condenses with thiocarbamide when the two substances are heated together at 110—125° for 1—2 hours; the product is *thiohydantoin-a-propionic acid*, $\begin{matrix}NH{:}C——S \\ \vert\quad\quad \\ NH{\cdot}CO\end{matrix}\!\!>\!CH{\cdot}CHMe{\cdot}COOH$, and the yield 80 per cent. of the theoretical. This acid melts at 224—225°; the *barium*, $(C_6H_7N_2SO_3)_2Ba$, and basic *copper*, $C_6H_7N_2SO_3{\cdot}Cu{\cdot}OH$, salts were prepared, and also the *hydrochloride*, $C_6H_8N_2O_3,HCl$. Boiling with aqueous barium hydroxide hydrolyses the acid to *thiohydroxypyrotartaric acid*, COOH·CH(SH)·CHMe·COOH; this was not obtained in well-defined crystals; when treated with benzylic chloride in alkaline solution, it yields a *benzyl* derivative which melts at 145° (uncorr.); its *barium* salt, $C_5H_6SO_4Ba + H_2O$, was also prepared. Cyanamide should also have been a product of the hydrolysis, but it could not be found; it is, however, possible to synthesise thiohydantoinpropionic acid from cyanamide and thiohydroxypyrotartaric acid. Thiohydantoin-a-propionic acid is oxidised by barium chlorate and hydrochloric acid to carbamide and a *sulphonic acid*, $COOH{\cdot}CH(SO_3H){\cdot}CHMe{\cdot}COOH$, identical with that obtainable from citraconic acid and ammonium hydrogen sulphite; the *barium* salt of this acid, $(C_5H_5SO_7)_2Ba_3 + 6H_2O$, was prepared. With ferric chloride, it gives a transient violet coloration, as do all thiohydroxy-acids; the ferric chloride acts as a carrier of oxygen, and the solution, when it has lost its violet colour, is found to contain *bisthiopyrotartaric acid*, $S_2[CH(COOH){\cdot}CHMe{\cdot}COOH]_2$, a syrup, the *barium* salt of which, $C_{10}H_{10}S_2O_8Ba_2 + H_2O$, was prepared.

Citraconic acid will also condense with substituted thiocarbamides. With symmetrical dimethylthiocarbamide, it yields *dimethylthiohydantoin-a-propionic acid*, which was obtained as an amorphous solid; the *barium* salt, $(C_8H_{11}N_2SO_3)_2Ba$, was prepared. With allylthiocarbamide, *allylthiohydantoin-a-propionic acid* is obtained as a syrup; the *barium* salt, $(C_9H_{11}N_2SO_3)_2Ba$, was prepared. With phenylthiocarbamide, it yields *phenylthiohydantoin-a-propionic acid*, which is crystalline, and melts at 214°. With diphenylthiocarbamide, it yields *diphenylthiohydantoin-a-propionic acid*, melting at 124°.

Attempts to make thiocarbamide condense with crotonic, cinnamic, and oleic acids, and with allylic alcohol, were unsuccessful. It is, thus, only with unsaturated dibasic acids that it will condense.

With bromomaleic acid, thiocarbamide yields *dehydrothiohydantoin-*

acetic acid, $\begin{matrix} NH:C\text{——}S \\ | \\ NH\cdot CO \end{matrix}\!\!>\!C:CH\cdot COOH$, which turns brown at 200°, and quite dark at 230—240°, without actually melting; sodium amalgam reduces it to thiohydantoinacetic acid, but this is for the most part hydrolysed by the alkali present to thiomalic acid (the benzyl derivative of which, $C_{11}H_{12}SO_4$, melts at 180—181°). It was hoped that the action of ammonia on it might lead to the formation of an amidothio-acid, which would have been of physiological interest; this is not the case, however. When bromomaleic acid is boiled with excess of aqueous potassium hydrosulphide, *hydrothiomaleic*, $COOH\cdot C(SH):CH\cdot COOH$, and some *thiodimaleic acid*, $S[C(COOH):CH\cdot COOH]_2$, are formed; the former is a syrup, and yields a *benzoyl* derivative, $C_{11}H_{10}SO_4$, melting at 175°; the latter melts and decomposes at 205°. The *benzyl* derivative of thioglycollic acid, $C_9H_{10}SO_2$, was also prepared; it melts at 60°. Thiohydantoin and β-methylthiohydantoin (from α-bromopropionic acid and thiocarbamide) unite with bromine (2 atoms) in acetic acid solution, forming *dibromine* additive products, $C_3H_4N_2SO,Br_2$ and $C_4H_6N_2SO,Br_2$; both of these are crystalline substances, and the second one melts at 176—177°; the bromine is entirely removed from them by aqueous silver nitrate or sulphurous acid. Methylhydantoin also unites with hydrogen bromide in acetic acid solution, forming a compound, $C_4H_6N_2SO,HBr$, which is readily decomposed by alkalis.

C. F. B.

Mercurocarbamide and its Salts. By G. RUSPAGGIARI (*Gazzetta*, 1897, **27**, i, 1—13).—Carbamide combines with mercuric salts, forming salts of a bivalent radicle, $CO(NHHg)_2$, which the author terms mercurocarbamide, and does not yield simple additive compounds; the reactions of the salts of this radicle with potassium iodide, sodium thiosulphate, and ammonium bromide are analogous to those of mercurammonium (Balestra, Abstr., 1893, ii, 278), carbamide being liberated in each case.

Mercurocarbamide hydroxide, $CO(NH\cdot Hg\cdot OH)_2$, was obtained by Liebig (*Annalen*, **85**, 289) by precipitating mercuric nitrate with an alkaline solution of carbamide, and may also be prepared by boiling yellow mercuric oxide with a solution of carbamide; Dessaignes (*Annalen*, **82**, 232) obtained a double compound of the composition $CO(NH\cdot Hg\cdot OH)_2,CO(NH_2)_2$ by boiling excess of concentrated carbamide solution with mercuric oxide. The *chloride*, $CO(NHHgCl)_2$, is obtained by adding a solution of carbamide in sodium hydrogen carbonate solution to mercuric chloride solution; it crystallises in microscopic, white pyramids, is insoluble in water, and is not affected by light. On boiling carbamide with mercuric chloride solution, a double *salt* of the composition $CO(NHHgCl)_2,CO(NH_2)_2,2HCl$ is formed and separates on cooling in long, colourless needles; it corresponds with the compound, $CO(NH_2)_2,HgCl_2$, described by Werther (*J. pr. Chem.*, **35**, 5).

Mercurocarbamide nitrate, $CO(NH\cdot Hg\cdot NO_3)_2$, separates as a gelatinous, white mass on mixing methylic alcoholic solutions of mercuric nitrate and carbamide; it is decomposed by water. The basic *nitrate*, $OH\cdot Hg\cdot NH\cdot CO\cdot NH\cdot Hg\cdot NO_3 + H_2O$, obtained by heating a dilute aqueous solution of mercuric nitrate with carbamide, crystallises in short

hexagonal prisms, has a feeble alkaline reaction, and is the compound obtained when Liebig's method of determining carbamide is properly carried out.

Mercurocarbamide sulphate, $CO\!:\!(NH{\cdot}Hg)_2\!:\!SO_4$, prepared from carbamide and mercuric sulphate, crystallises in tiny pyramids and is soluble in water. The *acetate*, $CO(NH{\cdot}Hg{\cdot}OAc)_2$, crystallises in thin, microscopic needles and is insoluble in the ordinary solvents.

W. J. P.

Triethylsulphine Metaaluminate. By UGO ALVISI (*Zeit. anorg. Chem.*, 1897, **14**, 302—308).—Triethylsulphine metaaluminate is formed by the action of a solution of triethylsulphine hydroxide on aluminium. Similarly to the solution of aluminium in sodium hydroxide, hydrogen is evolved in the action, and this reacts on the unaltered free base with formation of ethylic sulphide, ethane, and water, and also on the metaaluminate with the formation of ethylic sulphide, ethane, and aluminium hydroxide. When a concentrated solution of the aluminate is heated, it is completely decomposed into ethylic sulphide, ethylene, and aluminium hydroxide; the same decomposition also takes place when the solution is evaporated in a vacuum over calcium chloride or sulphuric acid; this decomposition is similar to that which the triethylsulphine hydroxide undergoes on heating, ethylic sulphide, ethylene, and water being formed. The above decomposition explains why triethylsulphine hydroxide is not obtained by the action of ethylic sulphide on ethylic alcohol, whereas the corresponding chloride or bromide is obtained by the action of ethylic sulphide on ethylic chloride, or bromide, or on ethylenic bromide. E. C. R.

Some new Constituents of Caucasian Naphtha. By WLADIMIR B. MARKOWNIKOFF (*Ber.*, 1897, **30**, 974—977).—A comparison of the boiling points of several fractions of Caucasian naphtha, with their specific gravities, showed certain irregularities; for instance, it was noticed that, between the fractions 58—48° and 48—46°, the sp. gr. fell from 0·712 to 0·666, and this could only be explained by supposing the presence of cyclic hydrocarbons in the mixture.

On nitrating the fractions 48—50° and 50—51°, a nitro-derivative was obtained which, on reduction, yielded an amine, which gave a characteristic benzoyl derivative, crystallising from alcohol in transparent, quadratic plates melting at 157·5—158·5°, and identical with the benzoyl derivative of amidocyclopentane prepared by Wislicenus' method. A large quantity of a crystalline acid was also produced during the process of nitration; this crystallised from water in large, quadratic plates melting at 96·5—97°, and corresponded in every respect with glutaric acid. Similarly, the fraction containing hexamethylene, on treatment with nitric acid, yielded adipic acid. It is, therefore, certain that cyclic hydrocarbons, containing no side chains, pass on oxidation with nitric acid into the corresponding dibasic acids.

Investigation of the fraction 90·5—98° showed the presence of a hydrocarbon, C_7H_{14}, containing a side chain; on nitration, this yielded a tertiary nitro-derivative of the formula $C_7H_{13}{\cdot}NO_2$, and boiling at 98—99° (40 mm.); the tertiary amine obtained on reduction boiled at

131—132°, and the tertiary alcohol was prepared from the amine by treatment with sodium nitrite at 144—145°. As a bye-product in the preparation of this alcohol, an unsaturated hydrocarbon of the formula C_7H_{12} was obtained. J. F. T.

The Benzene Nucleus. By WILHELM VAUBEL (*J. pr. Chem.*, 1897, [ii], **55**, 221—224. Compare Abstr., 1896, i, 646).—The author points out that his formula for benzene (Abstr., 1894, i, 325) admits of a certain oscillation of the groups within the molecule; this oscillation being granted, the formula no longer indicates the possibility of enantiomorphous bi-substitution derivatives. C. F. B.

Absorption of Nitrogen by Carbon Compounds under the influence of the Silent Electric Discharge. By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1897, **124**, 528—532).—The rate at which nitrogen is absorbed by benzene under the influence of the silent electric discharge (Abstr., 1895, ii, 469, 495, 498) is higher the more frequent the vibrations of the contact breaker. A Marcel-Deprez interrupter, with or without specially high frequency, gives better results than a Foucault interrupter. The maximum quantity of nitrogen absorbed by benzene is about 12 per cent. of the weight of the latter, and in presence of excess of benzene the absorption of chemical nitrogen is complete. In the case of atmospheric nitrogen, the absorption is incomplete, but the residue is smaller than the quantity of argon present with the nitrogen, because part of the argon is absorbed. The ratio of benzene to nitrogen, when the maximum absorption has taken place, is $3C_6H_6 : N_2$.

The empirical composition of the product corresponds with that of diphenylphenylenediamine, and it shows many of the properties of diamines of this class, mixed with products of condensation. It readily oxidises when exposed to air or oxygen, without any simultaneous liberation of nitrogen, and yields salts when treated with hydrochloric acid, the bases of these salts having odours which recall those of quinoline and the hydropyridine bases. The product formed with hydrochloric acid also yields ammonium chloride when heated. When the original product is heated, it yields large quantities of ammonia, together with benzene, water (resulting from oxidation by the air), a minute trace of aniline, and a bituminous liquid containing nitrogen compounds. When heated with special precautions to avoid previous contact with air, it yields ammonia, but no free nitrogen.

With carbon bisulphide, the absorption is more rapid than with benzene, and is complete in presence of an excess of bisulphide. With excess of nitrogen, the maximum quantity absorbed is 11·7 per cent. of the weight of the bisulphide, and the ratio is the same, $3CS_2 : N_2$. The product readily oxidises in contact with oxygen, and no appreciable quantity of nitrogen is liberated. When heated without having been in contact with air or oxygen, a certain proportion of the nitrogen is liberated, but the greater part remains in combination with the products of condensation, and it follows that the latter are more stable than the products formed by argon or helium.

Thiophen under similar conditions absorbs 8·6 per cent. of its weight

of nitrogen, the ratio in this case being $2C_4SH_4 : N$. The rate of absorption is lower than with carbon bisulphide. C. H. B.

Electrolytic Reduction of Aromatic Nitro-compounds. By WALTHER LÖB (*Chem. Centr.*, 1896, i, 901—902; from *Zeit. Elektrotechn. u. Elektrochem.*, 1896, 2, 529—534).—The author gives the following explanation of the fact that nitro-compounds, when reduced in alkaline solution, form mainly azo- and azoxy-compounds whilst in acid solution, hydrazo- and amido-compounds result. By the addition of water, a hydrated derivative, $RN(OH)_4$, is first formed, and this is not dissociated in solution, as neither hydrogen nor hydroxyl ions can be supposed to be formed. In the former case, the nitro-groups must be assumed to act as an acid and to form salts, whereas, in reality, the nitro-group cannot itself confer acidity, its function being limited to increasing the previous acidity of the molecule. The formation of hydroxyl ions is confined to substances of a basic character. If the alkaline solution of the hydrate $RN(OH)_4$ is kept at the negative pole by a diaphragm, the sodium ions which are liberated there react with the hydroxyl groups to form sodium hydroxide, and so may induce the following possible reactions, according to the number of hydroxyl groups which are separated from the nitrogen:—(1) The residues $R-N\equiv$, produced by separation of four hydroxl groups, unite to form an azo-compound; (2) an azoxy-compound is formed from the residues $RN(OH)\equiv$ obtained by the separation of three hydroxyl groups; (3) two hydroxyl groups are removed and the residues $RN(OH)_2=$ combine to form a nitroso-compound; (4) one hydroxyl group is separated and the residues, $RN(OH)_3-$, unite to form an unknown compound,

$$(NO)R\cdot O\cdot R(NO).$$

Experimental results with alkaline solutions show that only the first two possibilities come into consideration. The oxygen of the nitro-groups may also be supposed to be directly withdrawn by the action of sodium ions, the oxide then uniting with water to form sodium hydroxide, but on either assumption reduction is not effected by nascent hydrogen, but by the metal in virtue of its capability of forming hydroxyl ions. Hydrazo- and amido-compounds may also be produced in alkaline solution, but this occurs only after the reduction to azo-compounds is completed, when the nascent hydrogen derived from the action of sodium on water effects a further reduction. The quantities of azo- and azoxy-compounds obtained vary according to the conditions of concentration, a kind of equilibrium being established in each case when the sodium ceases to act on the azo-compound and hydrogen begins to be evolved and to produce the hydrazo-compound by reduction of the azo-compound. Reduction in acid solution is effected by means of hydrogen ions, which, after giving up their electric charges by separating hydroxyl groups from nitrogen, go again into the condition of ions, and finally bring about the conversion of azo-compounds into hydrazo- and amido-compounds.

To effect the reduction of nitrobenzoic acid in alkaline solution, a solution of equal weights of acid and sodium hydroxide in 20 parts of water is placed in the earthenware cathode vessel and this is immersed in dilute sodium hydroxide. The electrodes are of platinum, the

cathode being a cylinder 10 cm. high and 3 cm. diameter. At the ordinary temperature with 1—1·3 ampère at 6—6·5 volts, 5 grams of acid are reduced in 8—10 hours, hydrogen being liberated finally. Orthonitrobenzoic acid yields mainly orthazoxybenzoic acid with some orthohydrazobenzoic acid, the latter being separated from the former by conversion into orthodiamidodiphenic acid; meta- and para-nitrobenzoic acids give the corresponding azo-acids. Neglecting small losses of nitro-compounds at the positive pole, the reduction of the meta- and para-acids is quantitative. The ortho-acid yields 50 per cent. of azoxy-acid and 5—10 per cent. of diamidodiphenic acid.

Under the same conditions, orthonitrophenol gave 60 per cent. yield of orthodiamidophenol. E. W. W.

Electrolytic Oxidation of Paranitrotoluene. By KARL ELBS (*Chem. Centr.*, 1896, i, 902; from *Zeit. Elektrotechn. w. Elektrochem.*, 1896, 2, 522—523).—On electrolysis, paranitrotoluene is oxidised only to paranitrobenzylic alcohol, and not to the corresponding acid. A yellowish, crystalline substance was also obtained. From 15 grams of paranitrotoluene, a mean yield of 7 grams of nitrobenzylic alcohol was obtained. E. W. W.

Coloured Compounds obtained from Sodic Ethoxide and certain Aromatic Nitro-compounds. By C. LORING JACKSON and MARTIN H. ITTNER (*Amer. Chem. J.*, 1897, 19, 199—216).—A number of coloured compounds obtained by the action of an alcoholic solution of sodium ethoxide on various aromatic nitro-derivatives are described. The colours are given in the following table, in which the first column gives the name and formula of the substance from which the coloured compound is prepared, the second the colour obtained, and the third the stability of the colour:

Parabromodimetanitrotoluene, $C_6H_2Br(NO_2)_2Me$	Blue.	Seconds.
Anilidodinitrotoluene, $NHPh\cdot C_6H_2(NO_2)_2Me$	Green.	Seconds.
Amidophenyleneimidodinitrotoluene, $NH_2\cdot C_6H_4\cdot NH\cdot C_6H_2(NO_2)_2Me$	Green.	Seconds.
Tribromanilidodinitrotoluene, $C_6H_2Br_3\cdot NH\cdot C_6H_2Me(NO_2)_2$	Purple	Minutes.
Tribromamidophenyleneimidodinitrotoluene, $NH_2\cdot C_6HBr_3\cdot NH:C_6H_2Me(NO_2)_2$	Bluish purple.	Minutes.
Parabromodimetanitrobenzoic acid, $C_6H_2Br(NO_2)_2\cdot COOH$	Reddish purple.	Hours.
Ethylic parabromodimetanitrobenzoate, $C_6H_2Br(NO_2)_2\cdot COOEt$	Rose.	Hours.
Anilidodinitrobenzoic acid, $NHPh\cdot C_6H_2(NO_2)_2\cdot COOH$	Pansy purple.	Hours.
Ethylic anilidodinitrobenzoate, $NHPh\cdot C_6H_2(NO_2)_2\cdot COOEt$	Cherry red.	Hours.
Dinitranisic (dinitromethoxybenzoic) acid, $OMe\cdot C_6H_2(NO_2)_2\cdot COOH$	Reddish purple.	Hours.
Dinitroethoxybenzoic acid, $OEt\cdot C_6H_2(NO_2)_2\cdot COOH$	Reddish purple.	Hours.
Ethylic dinitroethoxybenzoate, $OEt\cdot C_6H_2(NO_2)_2\cdot COOEt$	Rose.	Hours.
Chrysanisic (dinitroamidobenzoic) acid $NH_2\cdot C_6H_2(NO_2)_2\cdot COOH$	Black.	
Ethylic chrysanisate, $C_6H_2\cdot NH_2\cdot(NO_2)_2\cdot COOEt$	Red.	

The coloured compound from dinitranisic acid was obtained as a heavy purple precipitate on adding light-petroleum to its alcoholic solution. On analysis, numbers were obtained agreeing with the formula $OMe \cdot C_6H_2(NO_2)_2 \cdot COONa,NaOEt$. On heating this substance to 110°, it suffers a loss of weight corresponding nearly to 1 molecule of alcohol.

The authors suggest that, in these compounds, a hydrogen atom between a nitro-group and the methyl or carboxyl group is the one replaced by sodium, from which the formulæ of the compound from dinitranisic acid would be $\begin{array}{l} OMe \cdot C \cdot (NO_2) : CH \\ \quad\;\; \| \qquad\qquad\;\; | \\ NO_2 \cdot C \cdot CNa : C \cdot COONa \end{array} + EtOH$

If this hypothesis is accepted, a strongly coloured compound might be expected, which would be decomposed by water or acid giving the original substance, and the compounds containing the negative carboxyl group would be more stable than those containing methyl, both of which points hold good in the compounds described. A further point in favour of this hypothesis lies in the authors' observation that the coloured compound from dinitranisic acid gives off alcohol on heating, whilst against it is the fact that it necessitates the following assumptions :—(*a*) The existence of 1 molecule of alcohol of crystallisation in each of the substances analysed, which is improbable in compounds derived from such different sources ; (*b*) that both alcohol and water of crystallisation can be contained in the same substance; (*c*) Lobry de Bruyn's observation that sodium does not act on trinitrobenzene even at the boiling point of xylene.

The coloured compound from bromodinitrobenzoic acid decomposes in contact with sodium ethoxide, yielding sodium bromide and dinitroethoxybenzoic acid, which combines with more sodium ethoxide forming the coloured compound of this acid. If the decomposition is allowed to go on spontaneously, sodium bromide and sodium dimetanitroparahydroxybenzoate are obtained. Similar decomposition products are produced from the compound formed by the action of sodium methoxide on bromodinitrobenzoic acid.

Dinitroethoxybenzoic acid, prepared by the action of hydrochloric acid on an alcoholic solution of ethylic chrysanisate (dinitroamidobenzoate), crystallises from alcohol in long, flat, colourless prisms, terminated by a single plane at an oblique angle. It melts at 192°, and is converted into dinitro-oxybenzoic acid on warming with dilute acids or alkalis. The *sodium* salt crystallises in easily soluble, yellow needles.

A. W. C.

Action of Zinc Ethyl on Phenylic Iododichloride. By ARTHUR LACHMANN (*Ber.*, 1897, **30**, 887—888).—As the result of some experiment conducted with these substances, the author states that zinc ethyl and phenylic iododichloride combine to form an additive product which is instantly decomposed by water, forming iodobenzene. In no case does the aqueous solution give a precipitate with potassium iodide.

J. F. T.

Derivatives of Phenylic Ether. By CARL HAEUSSERMANN and EUGEN BAUER (*Ber.*, 1897, **30**, 738—741. Compare Abstr., 1896, i, 676). —*Paradihydroxyphenylic ether*, which is obtained in small amount by

the action of nitrous acid on paradiamidophenylic ether, crystallises in white scales melting at 160—161°, and gives no coloration with aqueous ferric chloride. 2 : 2′-*Diamidophenylic ether* is obtained by the reduction of the corresponding nitro-compound, and crystallises in colourless needles melting at 60°; the *hydrochloride*, $O(C_6H_4{\cdot}NH_2)_2,2HCl$, crystallises in slender, white needles. When treated with sodium nitrite in acid solution, it yields a tetrazo-compound, which has not been isolated. 3-*Nitro-4-phenoxybenzoic acid* is prepared by heating 4-chloro-3-nitrobenzoic acid with potassium phenoxide (2 mol. prop.) at 140°; it forms indistinct, white crystals melting at 174—175°. The *barium* salt is very sparingly soluble in boiling water. The corresponding 3-*nitro-4-phenoxybenzenesulphonic acid* is prepared in a similar manner, and crystallises in white scales melting at 89—90°. The *potassium* salt crystallises in slender, white scales and the sparingly soluble *barium* salt in needles.

5-*Nitro-2-phenoxybenzoic acid* forms white, indistinct needles melting at 171—172°; the *barium* salt crystallises in white needles.

5-*Nitro-2-phenoxybenzenesulphonic acid* crystallises in white needles melting at 220°. A. H.

Some Derivatives of Dinitro-orthocresol. By PAUL CAZENEUVE (*Compt. rend.*, 1897, **124**, 154—156).—The following salts and derivatives of dinitro-orthocresol, $C_6H_2Me(NO_2)_2{\cdot}OH$ (1 : 3 : 5 : 2), are described. The *potassium* salt, $C_7H_5(NO_2)_2{\cdot}OK$, obtained by the addition of a slight excess of potash to a boiling solution of the dinitrocresol, crystallises in orange spangles; whilst the *ammonium* salt, $C_7H_5(NO_2)_2{\cdot}ONH_4 + H_2O$, prepared by saturating a solution of the dinitrocresol with ammonia, crystallises in golden yellow needles. The *barium* salt, $[C_7H_5(NO_2)_2O]_2Ba + 2H_2O$, is obtained by adding barium carbonate to a boiling solution of the dinitrocresol, and crystallises in orange needles which lose their water in a vacuum or when heated at 100°, the anhydrous salt being bright red; the *calcium* salt, $[C_7H_5(NO_2)_2O]_2Ca + H_2O$, is prepared in a similar manner; it crystallises in fine, yellow needles which lose their water at 100°, becoming bright red. All the above salts are soluble in water and alcohol.

The *acetyl* derivative, $C_7H_5(NO_2)_2{\cdot}OAc$, prepared by boiling the dinitrocresol with acetic anhydride, is colourless, insoluble in water, soluble in alcohol, ether, and benzene, and when crystallised from alcohol melts at 95°. *Nitroamino-orthocresol*, $NO_2{\cdot}C_7H_5(NH_2){\cdot}OH$ [= 3 : 5 : 2 or 5 : 3 : 2], prepared by boiling an ammoniacal, aqueous solution of the dinitrocresol with an excess of ammonium hydrosulphide, crystallises from boiling benzene in reddish-brown needles melting at 165°; it is insoluble in water, but soluble in alcohol, ether, and benzene. *Diamido-orthocresol*, $C_7H_5(NH_2)_2{\cdot}OH$ [= 3 : 5 : 2], could not be isolated, but its dihydrochloride is obtained by reducing dinitro-orthocresol by means of tin and hydrochloric acid. This salt, which crystallises in colourless needles, is soluble in alcohol and water, but insoluble in ether. A. C. C.

Halogen-derivatives of Thymol and Carvacrol. By LEO C. URBAN (*Chem. Centr.*, 1896, i, 1231; from *Pharm. Rev.*, 1896, **14**, 58).—The substitution product, $(C_{10}H_{12}OI)_2$, obtained by the action of iodine

on thymol, and known in commerce as aristol, can also be prepared by adding sodium hypochlorite to an alkaline solution of phenol containing an alkali iodide. The corresponding carvacrol derivative is a yellowish-brown powder melting at about 90°. The author has obtained another iodocarvacrol, a leather-coloured, amorphous powder soluble in ether, benzene, chloroform, and fatty oils, which begins to sinter at 170° and blackens at 200° without melting. The same compound is formed by adding a solution of iodine in potassium iodide to a solution of carvacrol in sodium hydroxide. The bromides of thymol and carvacrol, which, like the iodides, are derivatives of diphenol, are obtained in a similar way to the latter. Carvacrol bromide is a yellowish-grey or leather-coloured, almost odourless, powder.

E. W. W.

Constitution of Dibromo-ψ-cumenol Bromide and Similar Compounds. By KARL AUWERS (*Ber.*, 1897, **30**, 744—752. Compare Abstr., this vol., i, 34, and the two following abstracts).—Further investigation of dibromo-ψ-cumenol bromide has led the author to regard the formula proposed by Zincke, $CO{<}\substack{CMe{:}CBr \\ CBr{:}CMe}{>}CMeBr$, which he himself had formerly adopted, as unsatisfactory, evidence for the existence of a hydroxyl group in the compound having been obtained. When boiled with acetic anhydride, the bromide yields a *monacetate*, $C_9H_8AcBr_3O$, melting at 161°, in which the bromine atom appears to be more firmly combined than in the original compound. This monacetate reacts with sodium acetate, on continued boiling, to form the diacetate melting at 105—106°, previously described; the same compound is formed when the monacetate, $C_9H_8Br_2OAc{\cdot}OH$, which melts at 114° and is formed by the action of sodium acetate on the tribromo-compound, is boiled with acetic anhydride. When different acid radicles are introduced, however, the final di-acidyl derivatives are also different. Thus, when the monacetate melting at 161° is treated with silver isobutyrate, the compound $OAc{\cdot}C_9H_8Br_2{\cdot}O{\cdot}C_4H_7O$ is formed which melts at 79—80°. On the other hand, when the original tribromo-compound is treated with isobutyric anhydride, it yields the *isobutyrate*, $C_9H_8Br_3{\cdot}OC_4H_7O$, melting at 113°, and when this is digested with silver acetate, it is converted into the compound $OAc{\cdot}C_9H_8Br{\cdot}O{\cdot}C_4H_7O$, which is isomeric with that just described, but melts at 90—91°, and differs from it in crystalline form and other properties. The author suggests the formula

$$OH{\cdot}C{<}\substack{CMe{:}CBr \\ \text{———} \\ CBr{:}CMe}{>}C{\cdot}CH_2Br$$

as being in accordance with the various reactions of the substance, on the supposition that the hydroxyl group combined with the para-linked carbon atom has alcoholic and not phenolic functions. Monobromo-ψ-cumenol bromide, $C_9H_9Br(OH)Br$ (compare the following abstract), which melts at 81°, closely resembles the dibromo-compound in its behaviour towards acid radicles. The product of the action of acetic anhydride on the bromide melts at 92—93°, and when digested with silver isobutyrate yields the compound $OAc{\cdot}C_9H_9Br{\cdot}OC_4H_7O$ melting at 49—50°; the product of the action of isobutyric acid, on the other

hand, melts at 91°, and on treatment with silver acetate is converted into the compound $OAc·C_9H_9Br·O·C_4H_7O$, melting at 39—40°.

The investigation of this class of substances is being continued.

A. H.

Action of Bromine on Phenol-alcohols. By KARL AUWERS (*Ber.*, 1897, **30**, 753—755. Compare the foregoing abstract).—When bromine acts on a phenol-alcohol, it does not yield simple substitution products, but compounds which resemble dibromo-ψ-cumenol bromide in their behaviour. Paradimethylparahydroxybenzylic alcohol,

$$[Me_2 : CH_2·OH : OH = 1 : 4 : 6 : 3],$$

is converted by 1 mol. of bromine into *monobromo-ψ-cumenol bromide*, $C_9H_{10}Br_2O$, which crystallises in long, lustrous needles, melts at 81°, and is insoluble in alkalis. On reduction, it yields monobromo-ψ-cumenol melting at 32°, which is soluble in alkalis. Excess of bromine converts it into dibromo-ψ-cumenol bromide.

Orthohydroxy-alcohols show a similar reaction; thus saligenol yields a *bromo-compound*, $C_7H_6Br_2O$, which is insoluble in alkalis and melts at 98°. The author proposes to extend the reaction to a number of different substances belonging to this class. A. H.

A Class of Remarkable Nitration Products of the Phenols. By KARL AUWERS (*Ber.*, 1897, **30**, 755—759. Compare the two foregoing abstracts.)—Many phenols, especially such as contain several bromine atoms, resemble ψ-cumenol and its dibromo-derivative in their behaviour towards nitric acid (Abstr., 1896, i, 420) and yield characteristic nitration products which have not the properties of phenols. No such compound could be obtained from metaxylenol, but tribromometaxylenol yields a compound, $NO_2·C_6Me_2Br_3O$, which, like all the substances of this class, crystallises extremely well, and melts at 97° with violent evolution of gas.

When these nitration products are heated at 100° in any solvent of sufficiently high boiling point, oxides of nitrogen are evolved and crystalline compounds free from nitrogen are formed. The substance thus obtained from the nitration product of dibromo-ψ-cumenol $C_9H_{10}Br_2O_2$, is identical with one previously prepared by Zincke (Abstr., 1896, i, 214) by boiling dibromo-ψ-cumenol with dilute nitric acid, to which he gave the formula $CO{<}{\begin{smallmatrix}CMe\!:\!CBr\\CBr\!:\!CMe\end{smallmatrix}}{>}CMe·OH$. This substance appears to contain a hydroxyl group, since it yields a *monacetate*, which, however, has not been obtained quite pure. The nitration product would then be represented as the nitrite of this hydroxy-derivative, $C_6Me_2Br_2O·ONO$. The corresponding compound obtained from the nitration product of tribromometaxylenol melts at 173—174° and behaves in general like the foregoing. When crystallised from dilute acetic acid, it has the formula $C_8H_7Br_3O_2$, whereas when crystallised from light petroleum it has the formula $C_8H_5Br_3O$. The exact relation of these substances has not yet been determined. A. H.

Methylene Catechol [Ether]. By CHARLES MOUREU (*Bull. Soc. Chim.*, 1897, **15**, 654—656).—Equivalent quantities of catechol and

methylenic di-iodide were added to a solution of sodium ethoxide in alcohol, and the mixture was boiled for 60 hours. After distillation with steam, the product was freed from excess of methylenic di-iodide by treatment with potash. Methylene catechol ether is a colourless liquid, which boils at 172°—173°, and has sp. gr. = 1·202 at 0°.

M. W. T.

Conversion of Eugenol into Isoeugenol. By CHARLES GASSMANN (*Compt. rend.*, **124**, 38—40).—The sodium derivatives of ethylic, butylic, and amylic alcohols behave in a similar manner to the caustic alkalis in transforming eugenol into isoeugenol. With the ethoxide in alcoholic solution, it is necessary to boil for a long time, and even then the change is incomplete. The best results are obtained with sodium amyloxide in the presence of amylic alcohol, from which solvent the pure isoeugenol, boiling at 260°—262°, can readily be separated by fractional distillation. The same method may be employed for the conversion of safrole into isosafrole.

A. C. C.

Organo-mercuric Compounds derived from Benzylaniline. By L. PRUSSIA (*Gazzetta*, 1897, **27**, i, 14—18).—Pesci (Abstr., 1894, i, 248) has shown that benzylamine reacts with mercuric salts, forming salts of mercurobenzylamine, and that the mercury atom, in addition to being able to combine with basic nitrogen, can also enter an aromatic nucleus, probably in the para-position (Abstr., this vol., i, 36). In continuation of Pesci's work, the author shows that a bivalent radicle of the constitution $Hg<\begin{matrix}C_6H_4\cdot NH(C_7H_7)\\C_6H_4\cdot NH(C_7H_7)\end{matrix}>Hg$ can be formed, which he terms paramercurodiphenylenedibenzylmercurodiammonium. The *acetate* of this base, $Hg[C_6H_4\cdot NH(C_7H_7)\cdot OAc]_2Hg$, separates in thin, colourless needles on mixing alcoholic solutions of mercuric acetate and benzylaniline; after recrystallisation from benzene, it melts at 143·5—144°. It is soluble in chloroform, and on treatment with potash yields the *hydroxide*, $Hg[C_6H_4\cdot NH(C_7H_7)(OH)]_2Hg$; this crystallises with $3H_2O$ in small, colourless prisms which soften at 82·5° and melt with decomposition at 212·5°; it has an alkaline reaction and is decomposed by boiling water. The *chloride*,

$$Hg[C_6H_4\cdot NH(C_7H_7)Cl]_2Hg,$$

prepared by treating the acetate with calcium chloride, crystallises in brilliant laminæ melting at 173—174°. The *nitrate* is obtained as a crystalline, white powder on treating the hydroxide with nitric acid; it melts and decomposes at 150°.

On treating the hydroxide with sodium thiosulphate, it is converted into paramercurobenzylaniline, $Hg[C_6H_4\cdot NH(C_7H_7)]_2$, which crystallises from benzene in minute, white needles, and melts at 171·5° with partial decomposition.

W. J. P.

Bromophenacetine. By WILHELM VAUBEL (*J. pr. Chem.*, 1897, [ii], **55**, 217—219).—The substance obtained by boiling bromophenacetine with potash or acids is not a liquid, but a solid melting at about 20°; it cannot, therefore, be identical with Staedel's bromoparaphenetidine. If the amido-group is replaced by hydrogen, an oil is

obtained which is capable of taking up more bromine; the ethoxy-group here comes into play, and probably the formula, $NHAc\cdot C_6H_3Br\cdot OEt$ [$NHAc:Br:OEt = 1:2:4$], should be assigned to bromophenacetine.

C. F. B.

Differences between Aromatic Nitramines and Nitrosamines. By JOHANNES PINNOW (*Ber.*, 1897, 30, 833—843).—Although the author can give no method which is absolutely certain for distinguishing between nitramines and nitrosamines, yet, on the whole, Liebermann's nitroso-reaction serves in most cases; Bamberger, also (Abstr, 1893, i, 327; 1894, i, 238; 1895, i, 273), has shown that aromatic nitramines, when treated with mineral acids, yield the corresponding ortho- or para-nitranilines, whereas nitrosamines are decomposed by concentrated hydrochloric acid, or, better, by an alcoholic solution of aniline hydrochloride, and the nitroso-group is eliminated. Tolylnitramine, trinitrotolyl- and trinitrophenyl-methylnitramine do not give the nitroso-reaction, not even on warming with phenol. Tolylmethylnitramine gives the nitroso-reaction in the cold, but the colour is not intense and has a greenish tinge. Paranitrophenylnitramine and its methylic salt both in the cold and when heated, orthonitrotolylmethylnitramine in the cold and metanitrotolylnitramine on warming, give bluish-green colorations. Pure dinitrotolylmethylnitramine if heated gives a pure blue coloration, but no colour at all in the cold.

Paratolylmethylnitramine, obtained by the action of sodium methoxide, methylic alcohol, and methylic iodide on paratolylnitramine, crystallises in pale yellow prisms, melts at 74·5—75·5° and is readily soluble in all the usual organic solvents with the exception of cold, light petroleum. When treated with nitric acid, it yields metanitromethylparatoluidine (m. p. 83—84°).

Metanitroparatolylmethylnitramine is a golden-yellow, crystalline compound melting at 106—107° and readily soluble in most solvents, but only sparingly in cold alcohol or ether. It is not converted into dinitromethyltoluidine by the action of dilute acids, even on warning.

Orthonitroparatolylnitramine was obtained from nitrotoluidine by Bamberger's method; it crystallises in nearly colourless needles, melts at 91·5—92·5°, and is readily soluble in most solvents with the exception of water and light petroleum.

Orthonitroparatolylmethylnitramine.—Under this name, the author has previously (Abstr., 1896, i, 161) described a compound which is really a dinitromethyltoluidine. The true nitramine crystallises from alcohol in pale yellow prisms and melts at 82—83°.

Paranitrophenylmethylnitramine crystallises in yellowish needles and melts at 141·5—142·5° (uncorr.).

Trinitrotolylmethylnitramine, $C_6HMe(NO_2)_3\cdot NMe\cdot NO_2$[$Me:(NO_2)_3:N = 1:2:3:5:4$], is obtained by the action of fuming nitric acid on orthonitroparatolylmethylnitramine, on nitromethyldimethyltoluidine, or on nitrodimethyltoluidine. It crystallises from its chloroform solution in glistening, yellow needles, melts at 156·5—157° (uncorr.), and is sparingly soluble in ether or light petroleum, but readily in most hot solvents

Trinitromethyltoluidine was prepared from the above-mentioned trinitro-compound by Romburgh's method; it crystallises in orange-

coloured needles, melts at 129·5—130° (uncorr.), and is fairly readily soluble in most solvents. The corresponding *nitrosamine* crystallises in large, yellowish glistening plates and melts at 108—109° (uncorr.). It is readily decomposed even by dilute acids, and gives the Liebermann reaction. This nitrosamine was nitrated in acetic acid solution, the nitroso-group being eliminated. The product was a mixture of two *dinitromethyltoluidines*, which were separated by fractional crystallisation from chloroform and acetone. The one, γ, crystallises in long, orange-coloured plates, melts at 158·5—159·5° (uncorr.), and yields a *nitrosamine* melting at 128—128·5 (uncorr.); the other, β, crystallises in bright red prisms, melts at 184·5—185·5° (uncorr.), and is identical with the product obtained by the action of nitrous acid on orthonitrodimethyltoluidine, or by the oxidation of dinitrodimethyltoluidine (m. p. 104°); it yields a *nitrosamine* melting at 123—124° (uncorr.). Both dinitro-compounds, when further nitrated, yield the trinitrotolylmethylnitramine previously described. The author concludes with a few criticisms on Van Romburgh's work (*Rec. trav. chim.*, 1887, **6**, 365). J. J. S.

Addition of Methylic Iodide to Nitrosodimethylaniline. By LUDWIG KNORR (*Ber.*, 1897, **30**, 933—936).—Nitrosodimethylaniline reacts vigorously with methylic iodide to form a *methiodide*, which melts at about 125°. Boiling aqueous soda converts it into the same decomposition products as nitrosodimethylaniline itself, and hence the author concludes that it is probably a pseudomethiodide,

$NMe_2I:C_6H_4:N\cdot OMe$. A. H.

Acidyl Derivatives of the Nitrosamines. A Contribution to the Diazo-problem. By JULIUS W. BRÜHL (*Ber.*, 1897, **30**, 816—821).—The acidyl derivatives of the nitrosamines have been proved to behave in many respects as diazo-compounds (von Pechmann, *Ber.*, 1894, **27**, 703), and the author has now found a striking difference between the refraction equivalents of the group NO in alkyl and acidyl derivatives of the nitrosamines of the fatty series, which seems to indicate that the acidyl derivatives are also in reality diazo-derivatives. The values obtained for the refraction equivalent of the group NO in various nitrosamines of the fatty series are $\mathfrak{r}_\alpha = 5·33$ and $\mathfrak{r}_{Na} = 5·37$. The values of the same group in the nitrites, in which it is united with oxygen instead of nitrogen, are only a very little higher; $\mathfrak{r}_\alpha = 5·86$ and $\mathfrak{r}_{Na} = 5·91$. The value of the same group in nitrosoethylurethane, $EtO\cdot CO\cdot NEt\cdot N:O$ can be obtained by subtracting from the refraction equivalent of this compound that of the residue, $EtO\cdot CO\cdot NEt$– obtained from observations made on ethylurethane. In this way, the numbers are found to be $\mathfrak{r}_\alpha = 7·05$ and $\mathfrak{r}_{Na} = 7·07$. The author interprets this result as indicating that, in nitrosoethylurethane, the nitrogen atoms are probably united by multiple linkage, although the exact constitution cannot as yet be ascertained. Many of the reactions of nitrosoethylurethane can be much more simply expressed on this supposition than by means of the older formula. A. H.

Orthonitroparaphenylenediamine. By CARL BÜLOW and EUGEN MANN (*Ber.*, 1897, **30**, 977—988).—With dilute hydrochloric acid,

paranitrorthophenylenediamine forms a very stable mon-acid hydrochloride, and with concentrated hydrochloric acid an unstable di-acid compound, the latter being converted into the former on drying at 110—120°; both of these yield a diazo-compound only, and no tetrazo-compound, even when dry nitrous anhydride, N_2O_3, is passed through their alcoholic solutions. On benzoylation, a *monobenzoyl* derivative alone is formed, and similarly on acetylation, the *monacetyl* derivative alone is obtained, the compounds being the same as those produced by nitrating the diacetyl- or dibenzoyl-paraphenylenediamines and partially hydrolysing with alcoholic potash. By nitration, therefore, the nitro-group enters in the same position relatively to the benzoyl amido-group as the benzoyl group to the nitro-group, by the benzoylation of the nitro-base.

Orthonitromonacetylparaphenylenediamine is only a very feeble base, and does not form salts; it readily yields a diazo-compound, however, which, on combination, gives an azo-derivative yielding on hydrolysis a substance structurally isomeric with that produced by combining the diazo-derivative of the base with the same second component. The orthonitrodiacetyl compound, on reduction, yields paradiacetyltriamidobenzene, and this, on treatment with nitrite, passes into *diacetylamidobenzeneazimide*, $NHAc\cdot C_6H_4<\genfrac{}{}{0pt}{}{NAc}{N}>N$, a substance crystallising from glacial acetic acid in white needles melting at 165°. The corresponding *monacetyl* derivative separates from hot water in greyish-white needles melting at 241°.

All the compounds described have been previously prepared, the above two differing, however, in their melting points from those found by other investigators. J. F. T.

Diazotisation of Aniline. By STEFAN VON NIEMENTOWSKI and JOHANN VON ROSZKOWSKI (*Zeit. physikal. Chem.*, 1897, 22, 145—169).—The authors first determined the solubility and electrical conductivity of the aniline, aniline salts, and nitrites which were subsequently used. Of these, aniline chloride and sulphate are abnormal in their conductivity, giving at $v = 512$ no evidence of the attainment of a final constant value, a result probably due to hydrolytic decomposition. The migration velocity of the $\cdot NO_2$ ion was found to be 72·3, that is, a little higher than that of the nitric acid ion (= 65·1). In aqueous solution, silver nitrite and aniline yield, after many days, a precipitate of diazoamidobenzene and its silver salt, the yield increasing with the dilution. Analogous results were obtained with sodium and potassium nitrites, but the yields were smaller and the reaction slower. The reactions between aniline chloride and sulphate and the three nitrites were studied for different concentrations and proportions. In all cases, the reactions were similar to those represented by the equations

$$(NH_2Ph)_2,H_2SO_4 + AgNO_2 = H_2SO_4 + 2H_2O + Ph\cdot N_2\cdot NAgPh$$

and $(NH_2Ph)_2,H_2SO_4 + AgNO_2 = AgHSO_4 + 2H_2O + Ph\cdot N_2\cdot NHPh$, the first being the chief reaction. The yield was much larger than that obtained from the free base, probably owing to the increased concentration of the $C_6H_5\cdot NH$ ions. In acid solutions, aniline chloride and sodium nitrite yielded no diazoamidobenzene when the concentration of the acid was double that of the other compounds, whilst with the

other nitrites the quantity of this substance formed was greatly reduced by the addition of the second molecule of acid. L. M. J.

Stability of some Diazonium Compounds. By GIUSEPPE ODDO and G. AMPOLA (*Gazzetta*, 1896, **26**, ii, 541—548).—Oddo having shown (Abstr., 1895, i, 514) that whilst some diazonium compounds are stable at, and are formed at, higher temperatures, others are formed only at low temperatures, the authors have studied the influence of temperature on the formation of a number of diazonium derivatives; the process adopted was that of dissolving the base (1 mol.) in dilute hydrochloric acid (2 mols.), and after heating to the required temperature, adding concentrated sodium nitrite solution (1 mol.). After cooling and filtering, the quantity of diazonium compound formed was determined by adding alkaline β-naphthol solution or paranitraniline hydrochloride solution to the filtrate.

On diazotising at 100—105°, much diazonium compound is formed from meta- and para-nitraniline, parachloraniline, 1 : 3 : 4-dinitraniline and 1 : 2 : 5- and 1 : 3 : 6-nitrotoluidine, whilst little is obtained with meta-, chlor-, and brom-aniline, orthonitraniline, paramidobenzoic acid, and 1 : 5 : 2-nitrotoluidine. At 80—85°, much diazonium compound is obtained with the substances named above as giving little at 100—105°, whilst small yields are obtained with aniline, paratoluidine and α- and β-naphthylamine; at 60—65°, the four bases last named give good yields of diazonium compound, whilst orthotoluidine and paraxylidine give very poor ones. At 40—45°, paraxylidine in turn gives a good yield of diazonium compound.

It is evident from these results that the nature and position of the side chain groups in the base greatly influence the yield of diazonium compound; the presence of acidic radicles promotes the formation of such compounds at high temperatures, whilst that of alkylic radicles has the opposite effect. W. J. P.

Some New Hydroxyazo-compounds, and Derivatives of Triphenodioxazine. By KARL AUWERS and H. RÖHRIG (*Ber.*, 1897, **30**, 988—998).—For cryoscopic purposes, attempts were made to isolate oxyazo-compounds containing strongly negative groups in the para-position relatively to the hydroxyl, and since, as is well known, para-substituted phenols do not readily combine with diazo-chlorides, resort was had to the method of Bamberger and of Mills for the preparation of azo-compounds, namely, combining nitrosobenzene with the corresponding orthamido-derivative of the para-substituted phenol, and in this way many compounds of this class were prepared, although in every case about 20 per cent. of a bye-product was formed, readily separable, however, from the oxyazo-compound, owing to its insolubility in acetic acid; this was found to be a derivative of triphenodioxazine, and was evidently formed by the oxidation of the phenol.

Methylic metanitroparahydroxybenzoate, melting at 75—76°, and the corresponding *ethylic* salt melting at 69°, were first reduced by means of aluminium amalgam to the amido-compounds. *Methylic metamidohydroxybenzoate* crystallises best from benzene, from which it separates in slender needles and leaflets melting at 100—101°; the *ethylic* salt crystallises in glistening, flat prisms from hot chloroform, and melts at 110—111°, whilst the *free acid*, which has already been prepared by

other methods, crystallises in light-grey prisms containing $1H_2O$, and when dehydrated melts at 201°.

The condensation of these alkylic salts with nitrosobenzene takes place readily in the presence of acetic acid, forming *ethylic benzeneazoparahydroxybenzoate*, a finely crystalline compound, separating from dilute acetic acid in glistening, orange-red needles melting at 105—106°, and *methylic benzeneazoparahydroxybenzoate*, consisting also of orange-red needles melting at 116—117°; the corresponding *benzeneazohydroxybenzoic acid* crystallises from glacial acetic acid in yellow leaflets melting at 219·5—221°; at the same time, there is also formed *ethylic triphenodioxazinedicarboxylate*,

$$COOEt\cdot C_6H_3{<}{}^{N}_{N}{>}C_6H_2{<}{}^{O}_{N}{>}C_6H_3\cdot COOEt,$$

an insoluble compound, crystallising from nitrobenzene in dark-red, metallic leaflets and prisms; it dissolves in concentrated sulphuric acid, forming a deep blue solution. The *methylic* salt has precisely similar properties.

Benzeneazoparanitrophenol is produced when nitrosobenzene is allowed to condense with orthamidoparanitrophenol, formed by partially reducing dinitrophenol with ammonium sulphide; it crystallises from dilute acetic acid in orange-red leaflets melting at 150—151°; the *dinitrotriphenodioxazine* formed at the same time can be separated by boiling with glacial acetic acid, and consists of reddish-brown, metallic leaflets, dissolving in concentrated sulphuric acid with a blue-violet coloration.

Orthonitroparacyanobenzene, prepared from metanitroparahydroxybenzaldoxime, crystallises from absolute alcohol in prisms and needles melting at 169°, and passes, on boiling with acetic anhydride, into *acetylmetanitroparahydroxybenzonitrile* (or acetylorthonitroparacyanobenzene), $OAc\cdot C_6H_3(NO_2)\cdot CN$, a compound melting at 113—114°, and yielding, on hydrolysis, *orthonitrocyanophenol*; the latter crystallises from alcohol in yellow leaflets melting at 145°, and on reduction with aluminium amalgam, yields *orthamidoparacyanophenol*; this, when pure, crystallises from hot water in colourless leaflets melting at 157—158°; only traces of the condensation product of this compound with nitrosobenzene could be isolated, it being very unstable. *Dicyanotriphenodioxazine* forms dark-brown, metallic leaflets.

J. F. T.

Constitution of Certain Hydrazones. By PAUL C. FREER (*Ber.*, 1897, **30**, 736—738. Compare Abstr., 1895, i, 201).—Acetonephenylhydrazone is converted by bromine into acetoneparabromophenylhydrazone hydrobromide, the base of which readily oxidises in the air, forming *parabromobenzeneazoisopropylene*, which crystallises in large, yellow prisms, melts at 33°, and above this temperature decomposes very rapidly. When heated on a platinum spatula, it deflagrates and leaves a voluminous residue of carbon. It is converted by sodium amalgam into the original acetoneparabromophenylhydrazone, and by bromine into a *perbromide*, $C_9H_9N_2Br_6$, which crystallises in yellow rhombohedra, and melts and decomposes at 91°. This is accompanied by a second *perbromide*, $C_9H_9N_2Br_5$, which crystallises in needles, and

melts and decomposes at 102°. Both these compounds are converted by sodium amalgam into the bromhydrazone, whilst they are decomposed when boiled with water, with separation of bromine. All these reactions characterise the original compound as an aliphatic azo-derivative.

Acetophenoneparabromophenylhydrazone behaves in a similar manner, yielding by spontaneous oxidation in the air a *substance* which crystallises well, melts and decomposes violently at 48°, and is converted by bromine into a crystalline *perbromide* melting at 180°.

In contrast with these compounds, the substance which is considered by Bender (Abstr., 1888, 53) to be ethylic β-phenylazocrotonate yields no perbromide when treated with bromine, but is converted into resinous products with evolution of hydrogen bromide. A. H.

New Method of Preparing Thiosemicarbazides. By MAX BUSCH and HERM. RIDDER (*Ber.*, 1897, **30**, 843—849).—It has already been shown (Abstr., 1896, i, 581) that phenylthiocarbazinic acid, when heated with aniline at 110°, readily forms diphenylthiosemicarbazide.

1-*Phenyl*-4-*orthotolylsemicarbazide*, $NHPh\cdot NH\cdot CS\cdot NH\cdot C_6H_4Me$, can readily be formed in a similar manner; it crystallises in small, white needles, and melts at 153°.

1-*Phenyl*-4-*dipropylthiosemicarbazide*, $NHPh\cdot NH\cdot CS\cdot NPr_2$, crystallises from light petroleum or from dilute alcohol in glistening needles, melts at 104°, and is readily soluble in the usual solvents with the exception of water.

1-*Phenyl*-4-*diamylthiosemicarbazide* melts at 99—100°, and *phenyldibenzylthiosemicarbazide* at 139°; the latter is but sparingly soluble in light petroleum and in ether.

1:4-*Diphenyl*-4-*methylthiosemicarbazide*, $NHPh\cdot NH\cdot CS\cdot NMePh$, melts at 142° and 4-*piperidyl*-1-*phenylthiosemicarbazide* at 120°. Ammonium phenylthiocarbazinate, obtained by passing ammonia into an ethereal solution of the acid, melts at 117·5°, and is readily soluble in alcohol and water. In the preparation of the salt, it is necessary to pass in the ammonia as rapidly as possible, since the acid readily decomposes even in ethereal solution into carbon bisulphide and phenylhydrazine. Phenylthiosemicarbazide could not be obtained by heating the ammonium salt. The method here given cannot be recommended for the preparation of thiosemicarbazides from primary amines, as the yield is too poor (20—25 per cent.), and the compounds can be obtained more readily by means of the thiocarbimides. The method is useful, however, in the case of secondary amines, the thiosemicarbazides of which cannot be prepared by other means. J. J. S.

Formation of Vanillin from Vanillolycarboxylic Acid. By CHARLES GASSMANN (*Compt. rend.*, 1897, **124**, 38).—When 1 part of vanillolycarboxylic acid is boiled with 2 parts of aniline until the disengagement of carbonic anhydride ceases, a compound is formed having the formula $OMe\cdot C_6H_3(OH)\cdot CH\colon NPh$ [= 3 : 4 : 1], from which vanillin can be separated by heating with 50 per cent. sulphuric acid. From acetylvanilloylcarboxylic acid, by the same method, acetyl vanillin may be obtained. A. C. C.

Action of α-Bromopropionic Chloride on Benzene in presence of Aluminium Chloride. By A. COLLET (*Bull. Soc. Chim.*, 1897, [iii], 15, 715—717. Compare this vol., i, 73).—By the action of aluminium chloride on α-bromopropionic chloride in excess of benzene at 100°, the author obtains the ketone CHMeBr·COPh. It is a liquid which boils at 135—137° under 20 mm. pressure, and has a sp. gr. 1·42 at 15°. When oxidised with permanganate, it gives benzoic acid, and when treated with aniline in the cold, the anilide NHPh·CHMe·COPh is obtained in crystals melting at 98°. The anilide of the bromopropiophenone, obtained by Pampel and Schmidt by direct bromination of propiophenone, melts at 38°. M. W. T.

Action of Acetic Chloride and Benzoic Chloride on Styrene in presence of Zinc Chloride. By ISSAR TAGER (*Chem. Centr.*, 1896, ii, 354, from *Diss. Dorpat*, 1896).—*β-Chlorobenzoylacetone* and *benzylideneacetone* are formed by the action of acetic chloride on styrene in presence of zinc chloride. The hydrazone of the former is crystalline but very unstable, decomposing very easily into substances which give the pyrazolone reaction. By the action of hydrochloric acid, it breaks down into acetone, benzaldehyde, and phenylhydrazine. Benzylideneacetone gives a hydrazone, which at the moment of formation probably changes into a pyrazolone. β-Chlorobenzoylacetone forms a crystalline oxime, benzylideneacetone a liquid oxime which unites with bromine to form a crystalline substance. By treating a mixture of both ketones with moist silver oxide, a ketonic alcohol is obtained.

Benzoic chloride reacts with styrene in a similar way to acetic chloride. E. W. W.

Electrolysis of Benzoic Acid. By WALTHER LÖB (*Zeit. Elektrochem.*, 1896, 3, 3).—A somewhat alkaline solution of sodium benzoate is electrolysed with a current density of 0·209 ampère per sq. cm. at the cathode and 0·151 at the anode, the temperature not exceeding 40°. After decomposition of the greater part of the benzoic acid, it is possible to isolate from the solution a substance having the composition $C_5H_5NaO_6$ which crystallises in large plates. It softens at 240°, but is not liquid at 285°, dissolves readily in water, alcohol, glacial acetic acid, soda, or dilute acids, sparingly in amylic alcohol, ether, benzene, light petroleum, chloroform, ethylic acetate, and fuming hydrochloric acid. In concentrated sulphuric acid, it dissolves without coloration. The aqueous solution gives no precipitates with metallic salts. Iodine does not attack it at 180—190°, but bromine reacts with it, yielding a product melting at 181°, the yield of this substance being about 1 per cent. of the benzoic acid used. The gases evolved during the electrolysis consist of carbonic anhydride, carbonic oxide, and small quantities of acetylene. A small but easily recognised quantity of benzaldehyde is formed, but neither aromatic hydrocarbons nor fatty acids could be detected. T. E.

Reduction of Phenolcarboxylic Acids. By ALFRED EINHORN (*Annalen*, 1897, **295**, 173—187. Compare Abstr., 1896, i, 45 and 530). —The cresotic acids have been included in the experiments dealing

with the behaviour of phenolcarboxylic acids towards sodium and amylic alcohol; the ortho-, meta-, and para-compounds yield α-, β-, and γ-methylpimelic acids respectively. Employment of the acids themselves, however, results in the production of a very small yield; this difficulty is overcome by reducing brominated cresotic acids, an artifice which raises the yield to 70 per cent. of that required by theory.

[With HERMANN EHRET].—α-Methylpimelic is produced in small quantity when orthocresotic acid is reduced with sodium and amylic alcohol; it is more convenient, however, to reduce *dibromorthocresotic acid*, which crystallises from dilute alcohol in white needles resembling ammonium chloride, and melts at 232°. α-Methylpimelic acid, which has been already described by Zelinsky and Generosoff (Abstr., 1896, i, 350), is also obtained on reducing α-hydroxyuvitic acid. The *calcium* salt is a white precipitate formed on adding alcohol to the aqueous solution; the *diethylic* salt boils at 132—137° under a pressure of 23 mm., and the *anilide* crystallises from dilute alcohol in lustrous, white needles melting at 166—167°.

Dibromometacresotic acid cystallises from dilute alcohol in white needles, and melts at 234°; reduction with sodium and amylic alcohol converts it into *β-methylpimelic acid*, $COOH\cdot CH_2\cdot CHMe\cdot[CH_2]_3\cdot COOH$, which melts at 48—50°, and distils without undergoing change. The *calcium* salt crystallises in leaflets; the *diethylic* salt boils at 155—160° under a pressure of 25 mm., and the *anilide* melts at 136°.

β-Methylcyclohexanone, $CHMe<\begin{matrix}CH_2-CO\\CH_2\cdot CH_2\end{matrix}>CH_2$, is obtained by heating β-methylpimelic acid with soda lime, and forms a colourless liquid having a faint odour of peppermint; it boils at 162—164°, and is not identical with the cyclic ketone obtained by Wallach on heating pulegone with anhydrous formic acid (Abstr., 1896, i, 309). The *semicarbazone* melts at 191—192°, and the *dibenzylidene* derivative crystallises from methylic alcohol in yellow needles, and melts at 121—122°. The author regards the synthetical product as the racemic modification of the ketone, β-methylcyclohexanone from pulegone being the dextrogyrate form.

Dibromoparacresotic acid crystallises from dilute alcohol in prismatic needles, and melts at 204—205°; reduction converts it into *γ-methylpimelic acid*, $CHMe(CH_2\cdot CH_2\cdot COOH)_2$, which melts at 56—57° and distils without decomposing. The *calcium* salt is precipitated from the aqueous solution by alcohol, the *diethylic* salt boils at 160—167° under a pressure of 31 mm., and the *anilide* crystallises from dilute alcohol in silky, white needles and melts at 158—159°.

γ-Methylcyclohexanone, $CHMe<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>CO$, is obtained when γ-methylpimelic acid is distilled with lime; it is a colourless oil, which boils at 163—165°, and forms a crystalline compound with sodium hydrogen sulphite. The *semicarbazone* melts at 199°. M. O. F.

Hexahydroanthranilic Acid. By ALFRED EINHORN (*Annalen*, 1897, **295**, 187—222. Compare Einhorn and Meyenberg, Abstr., 1894, i, 591).—[With BENJAMIN S. BULL and ALFRED GERNSHEIM.]—*Orthourethanehexahydrobenzoic acid*, $COOH\cdot C_6H_{10}\cdot NH\cdot COOEt$, ob-

tained by agitating an aqueous solution of sodium hexahydroanthranilate with ethylic chlorocarbonate, crystallises from ethylic acetate in colourless needles melting at 158·5°; the *ethylic* salt forms needles, and melts at 59—60°.

Benzoylhexahydroanthranilic acid, $COOH \cdot C_6H_{10} \cdot NHBz$, crystallises from dilute alcohol in colourless needles, and melts at 220—221°; the *ethylic* salt melts at 131°. *Ethylic benzenesulphonehexahydroanthranilate*, $COOEt \cdot C_6H_{10} \cdot NH \cdot SO_2Ph$, is obtained by the action of benzenesulphonic chloride on ethylic hexahydroanthranilate, and crystallises from a mixture of benzene and petroleum in white prisms melting at 93°.

[With B. S. BULL.]—When ethylic hexahydroanthranilate is exposed to air, it becomes converted into the acid in a few days; the *platinochloride* of the salt crystallises in orange-coloured scales, and explodes at 219—220°.

Orthoparadinitrophenylhexahydrophenylamineorthocarboxylic acid,

$$C_6H_3(NO_2)_2 \cdot NH \cdot C_6H_{10} \cdot COOH,$$

is obtained by heating hexahydroanthranilic acid, dinitrochlorobenzene, and potassium carbonate with dilute alcohol in a reflux apparatus until a portion of the liquid dissolves completely in alkali after removing the alcohol; it forms orange-coloured crystals, and melts at 241°. The *ethylic* salt crystallises in greenish-yellow needles, and melts at 136—137°.

Ethylic orthophenylthiouraminohexahydrobenzoate,

$$NHPh \cdot CS \cdot NH \cdot C_6H_{10} \cdot COOEt,$$

produced on adding phenylcarbimide to a solution of ethylic hexahydroanthranilate in acetone, crystallises from a mixture of acetone and petroleum in microscopic needles melting at 162—163°.

Ethylic orthothiocarbamidehexahydrobenzoate,

$$CS(NH \cdot C_6H_{10} \cdot COOEt)_2,$$

is obtained by heating ethylic hexahydroanthranilate with carbon bisulphide and absolute alcohol in a reflux apparatus on the water bath, and crystallises from 80 per cent. alcohol in white needles melting at 133°.

Hexahydroanthranilamide, $NH_2 \cdot C_6H_{10} \cdot CONH_2$, is not prepared by the action of phosphorus pentachloride on hexahydroanthranilic acid and subsequent treatment with ammonia, but from ethylic hexahydroanthranilate by acting on it with methylic alcoholic ammonia in sealed tubes at 145° during 7 hours; it crystallises from absolute alcohol in slender needles, and melts at 153·5°. The *platinochloride* forms pale orange crystals, and explodes at 234—237°; the *hydrochloride* and *hydrobromide* crystallise from absolute alcohol in prismatic needles, and melt at 251—252° and 257—259° respectively.

The compound, $C_7H_{12}N_2O$, obtained by the action of alkali hypobromite on the amide (Abstr., 1896, i, 472) forms a *nitroso*-derivative, which is precipitated from chloroform by petroleum, and explodes at 65°; the *benzoyl* derivative crystallises in small, slender needles, and melts at 187°.

Hexahydro-orthophenylenediamine (orthohexamethylenediamine) is obtained from the intermediate compound, $C_7H_{12}N_2O$, by the action of hot, concentrated hydrochloric acid; it is an oily liquid of ammoniacal odour, absorbs atmospheric carbonic anhydride, solidifies in a freezing

mixture, and boils at 183—185° under a pressure of 720 mm. The dihydrochloride (*loc. cit.*) crystallises on adding ethylic acetate to the solution in dilute alcohol, and does not melt below 280°; the *dihydrobromide* behaves in the same way, whilst the *hydrobromide* crystallises from absolute alcohol in small plates, and melts at 209—214°. The *platinochloride* is pale yellow, and the *picrate* forms small, yellow needles, becoming black between 210° and 250°; the *carbamate* separates as a white powder when carbonic anhydride is passed into an ethereal solution of the base, and sublimes at 170—178°. The *diacetyl* derivative sublimes without decomposing, and melts at 260—261°, whilst the *dibenzoyl* derivative crystallises from glacial acetic acid in needles, and does not melt below 280°; the *dibenzenesulphonic* derivative melts at 155°.

Hexahydro-orthophenylenecarbamide, $C_6H_{10}<{NH \atop NH}>CO$, is produced when phosgene is passed into a solution of hexahydro-orthophenylenediamine in excess of caustic soda; it crystallises from ethylic acetate in quadratic plates or prisms, reduces Fehling's solution, sublimes without decomposing, and melts at 230—231°.

μ-Phenylhexahydrobenzylbenzimidazole, $C_6H_{10}<{N(CH_2Ph) \atop \overline{}N}\geqslant CPh$, is obtained on adding benzaldehyde (2 mols.) to a solution of hexahydro-orthophenylenediamine which has been neutralised with sodium carbonate; it crystallises from alcohol in short, white needles, and melts at 132·5°.

B-*Hexahydro-αβ-diphenylquinoxaline*, $C_6H_{10}<{N:CPh \atop N:CPh}$, prepared by heating hexahydro-orthophenylenediamine with an alcoholic solution of benzil (1 mol.) on the water bath, crystallises in sulphur-yellow, prismatic needles melting at 167—169°, and distilling without change; concentrated hydrochloric and sulphuric acids dissolve it with development of a red coloration, and water precipitates benzil from the solutions. The quinoxaline derivative is also produced from hexahydro-orthophenylenediamine and benzoin, and in this respect affords a parallel with αβ-diphenyl-γδ-dihydropyrazine, which is the product of the action of ethylenediamine alike on benzil and benzoin.

B-*Tetrahydro-αβ-phenanthra*-n-*dihydroquinoxaline*,

$$C_6H_8<{NH\cdot C\cdot C_6H_4 \atop NH\cdot C\cdot C_6H_4},$$

is obtained by heating hexahydro-orthophenylenediamine with phenanthraquinone (1 mol.) dissolved in methylic alcohol, and crystallises in orange needles, melting at 145·5°; the solution in concentrated hydrochloric or sulphuric acid is green. The *monacetyl* derivative becomes red at 140°, and melts at 163—165°.

B-*Tetrahydro-αβ-phenanthraquinoxaline*, $C_6H_8<{N\cdot C\cdot C_6H_4 \atop N\cdot C\cdot C_6H_4}$, is produced when the foregoing compound is heated with glacial acetic or mineral acids, and crystallises in pale yellow needles, melting at 202—204°; the solution in concentrated sulphuric acid is brownish-red. M. O. F.

Action of Ethyloxalic Chloride [Ethylic Chloroglyoxylate] on ψ-Cumene and on Mesitylene. By E. (? LOUIS) BOUVEAULT

(*Compt. rend.*, 1897, **124**, 156—158. Compare Abstr., 1896, i, 551, 616, 649, 650).—ψ-Cumene readily reacts with ethylic chloroglyoxylate in presence of aluminium chloride, forming *ethylic ψ-cumylglyoxylate*, a yellow liquid of disagreeable odour, and boiling at 175°—176° (10 mm.). ψ-Cumylglyoxylic acid separates from carbon bisulphide in colourless crystals melting at 76°, and is identical with the acid obtained by Claus by the oxidation of acetyl-ψ-cumene. When its solution in concentrated sulphuric acid is poured into water, durylic acid is obtained. When heated with aniline, it gives a yellow crystalline *phenylimide* boiling at 206° (10 mm.) and melting at 62°. When boiled with dilute sulphuric acid, this phenylimide yields the corresponding *aldehyde*, $C_6H_2Me_3{\cdot}COH$, which forms colourless crystals melting at 43·5° and boiling at 121° (10 mm.); from this, the *hydrazone*, $N_2(\colon CH{\cdot}C_6H_2Me_3)_2$, melting at 181° and soluble in benzene and light petroleum, is obtained. In the action of ethylic chloroglyoxylate on ψ-cumene, no isomerides of ψ-cumylglyoxylic acid are formed. Ethylic mesitylglyoxylate is obtained in a similar manner to the corresponding ψ-cumene derivative as a yellow liquid boiling at 164—165° (11 mm.); the corresponding acid, crystallised from carbon bisulphide, melts at 117—118°, and is identical with the acid obtained by Claus. When heated at 100° with a solution of hydrazine hydrate, it yields the *acid*, $N_2[\colon C(C_6H_2Me_3){\cdot}COOH]_2 + H_2O$, melting at 200° and giving rise, with loss of carbonic anhydride, to the hydrazone of the corresponding aldehyde. The *phenylimide* forms yellow crystals melting at 48—49°, boiling at 202° (10 mm.), and is converted by dilute sulphuric acid into the corresponding aldehyde melting at 14° and boiling at 117° (10 mm.), which has already been described by Feith (Abstr., 1892, 329), who only obtained it as a liquid. Its hydrazone forms yellow crystals melting at 171°, and is almost insoluble in ether, but fairly soluble in hot benzene.

Acetylmesitylene does not react with hydrazine hydrate.

A. C. C.

Nitrophenoxy-acids. By ATTILIO PURGOTTI (*Gazzetta*, 1896, **26**, ii, 554—559).—Although sodium chloracetate reacts with sodionitrophenol, giving a nitrophenoxyacetic acid, it does not react with picric chloride, and attempts which the author has made to bring about a similar reaction between picric chloride and the ethylic sodioglycolate or ethylic lactate were unsuccessful. Picric chloride, however, reacts with methylic sodiosalicylate in boiling toluene solution giving *methylic picrylsalicylate*, $C_6H_2(NO_2)_3{\cdot}O{\cdot}C_6H_4{\cdot}COOMe$, which forms yellow crystals melting at about 139°; attempts to obtain the free acid were unsuccessful, as when hydrolysis occurs picric and salicylic acids are formed.

Picrylsalicylaldehyde, $C_6H_2(NO_2)_3{\cdot}O{\cdot}C_6H_4{\cdot}COH$, is obtained by boiling salicylaldehyde and picric chloride with soda in alcoholic solution; it forms small, yellow crystals melting at 154°, and is readily converted into a *phenylhydrazone*, $C_6H_2(NO_2)_3{\cdot}O{\cdot}C_6H_4{\cdot}CH\colon N{\cdot}NHPh$, which crystallises in yellow needles melting at 217°. W. J. P.

Azo-opianic Acid. By ADOLPH CLAUS and FRANZ PREDARI (*J. pr. Chem.*, 1897, [ii], **55**, 171—185).—The substance that is still often

described under this name, for example, in the third edition of Beilstein's *Handbuch*, and is obtained by the reduction of nitro-opianic acid with stannous chloride, has long been shown to be in reality an anhydride (resembling anthranil in character) of orthamidohemipinic acid. The true *azo-opianic acid*,
$N_2[C_6H(OMe)_2(CHO)\cdot COOH]_2$ $[N:(OMe)_2:COOH:CHO = 1:3:4:5:6]$ is obtained by reducing nitro-opianic acid in aqueous solution with $2\frac{1}{2}$ per cent. sodium amalgam at 0°. It is yellow, and melts and decomposes at 174°; the salts are yellow to brown in colour, and the *sodium*, $C_{20}H_{16}N_2O_{10}Na_2 + 3H_2O$; *potassium*, $C_{20}H_{16}N_2O_{10}K_2 + 6H_2O$, and *barium* salts are very soluble in water, whilst the *copper*, *iron*, *lead*, $C_{20}H_{16}N_2O_{10}Pb$, and *silver* salts form flocculent precipitates. With phenylhydrazine, the acid condenses to red *azo-opianic-phenylhydrazide*, $N_2\left[C_6H(OMe)_2{<}\begin{matrix}CO\cdot NPh\\ CH:N\end{matrix}\right]_2$, melting at 258°, which is at the same time a hydrazone; with hydroxylamine, it yields yellow *azohemipinimide* $N_2[C_6H(OMe)_2{<}\begin{matrix}CO\\ CO\end{matrix}{>}NH]_2$, melting and decomposing at 250°; with acetic anhydride and sodium acetate, it yields yellow *azo-opianic anhydroacetate*, $N_2[C_6H(OMe)_2{<}\begin{matrix}CO\\ CH(OAc)\end{matrix}{>}O]_2$, melting at 210°.

When azo-opianic acid (1 mol.) is suspended in a little water, or dissolved in a little acetic acid, and then boiled with fuming nitric acid (1 mol.), a reddish, crystalline substance is obtained which is still unmelted at 280°, and apparently has the composition $C_{20}H_{15}N_3O_9$. When the acid is heated with strong hydrochloric acid, a colourless, crystalline substance is obtained which does not melt at 300°, and appears to have the composition $C_{10}H_9NO_5$. C. F. B.

Constitution of Tannic Acid. By HUGO SCHIFF (*Gazzetta*, 1897, **27**, i, 90—96).—The author having shown that the natural tannic acid is dextrorotatory (Abstr., 1896, i, 370), suggested for it the following constitution, which contains six hydroxyl groups and an asymmetric carbon atom, $\begin{matrix}C(OH)\cdot C(OH)\text{---}C\cdot OH & CH\cdot C(OH):C(OH)\\ CH\text{---}C(COOH)\cdot C\text{--}CO\text{--}C & \text{---}CH{=}C(OH)\end{matrix}$.
On acetylating the acid by various methods, a dextrorotatory *pentacetyltannic acid* is obtained which is insoluble in water, and has about the same specific rotation as natural tannic acid; the compositions of the cupric, ammoniocupric, lead, and mercuramine salts (Abstr., 1875, 1197) also point to the existence of only five hydroxyl groups in tannic acid.

Gallic acid gives a good yield of rufigallol when heated with concentrated sulphuric acid at 100°, and if the ketonic nature of tannic acid as expressed by the above constitution is correct, the latter acid should yield rufigallol with even greater readiness. On heating tannic acid with concentrated sulphuric acid at 100°, however, carbonisation occurs and sulphurous anhydride is evolved; a little rufigallol is indeed formed, but only from the gallic acid into which the tannic acid is partially converted. Tannic acid gives no hydrazone, but only a resinous

substance when treated with phenylhydrazine under various conditions.

The author was unable to synthesize tannic acid by B. Hunt's method (Abstr., 1885, 1228) of heating bromoprotocatechuic acid with potassium gallate and a little alcohol or water at 100—105°; this synthesis, therefore, cannot be used in support of the older formula for tannic acid which contains no asymmetric carbon atom.

W. J. P.

Some Ethylic Salts of Phthalic and Tetrachlorophthalic Acid. By RICHARD E. MEYER and A. JUGILEWITSCH (*Ber.*, 1897, **30**, 780—788).—The object of these experiments was to determine whether the ethylic salts obtained by the action of alkylic iodides on silver phthalate were isomeric or identical with these formed by the action of the corresponding alcohol on phthalic chloride, and thus to indicate the symmetrical or asymmetrical structure of the latter. In every case examined, the two compounds were found to be identical.

Benzylic phthalate crystallises from alcohol in thick prisms, melting at 42—43°, the *benzylic hydrogen salt* melting at 102—104°.

Paranitrobenzylic phthalate separates from benzene in long needles melting at 154—155°.

Cetylic phthalate crystallises from alcohol in slender needles melting at 42—43°.

Benzylic tetrachlorophthalate crystallises from methylic alcohol in colourless needles melting at 92—93°.

Paranitrobenzylic tetrachlorophthalate separates from hot benzene in long needles melting at 179—180°, whilst *cetylic tetrachlorophthalate* is precipitated from its ethylic acetate solution by means of methylic alcohol as fine leaflets melting at 49—50°.

J. F. T.

Addition of Halogens and Halogen Acids to Unsaturated Sulphones. By JULIUS TROEGER and A. HINZE (*J. pr. Chem.*, 1897, [ii], **55**, 202—217).—The unsaturated sulphones were of the type $R\cdot SO_2\cdot CH_2\cdot CH\colon CH_2$, and were obtained by the action of allylic bromide on sulphinates. Either alone or in solution in carbon tetrachloride, they readily absorb chlorine, forming dichlorides, and, when dissolved in glacial acetic acid, they unite with bromine, yielding dibromides, but they will not unite with iodine. They also unite with hydrogen bromide or iodide, yielding compounds $R\cdot SO_2\cdot CH_2\cdot CHX\cdot CH_3$ when heated for several hours with a solution of the gas in glacial acetic acid, at 120° and 140° respectively; with hydrogen chloride, they will not unite, even at 200°. It is already known that heating these dibromides with water for 20—40 hours at 120—140° sometimes leads to the formation of a glycol, but, in the case of β-naphthylallylsulphone dibromide, to the replacement of the two atoms of bromine by one of oxygen; the α-naphthyl isomeride is now found to behave like the β-compound, whereas paratolylallylsulphone dibromide yields a glycol. The new compounds described are enumerated below, and their melting points given.

Phenylallylsulphone dichloride, 72—73°. *Paratolylallylsulphone dichloride*, 78—79°. *Naphthylallylsulphone dichlorides*; α, oil; β, between 103° and 110°. *α-Naphthylallylsulphone dibromide*, oil. *Monobromo-*

propylphenylsulphone, *monobromopropylparatolylsulphone*, *monobromopropyl-α-naphthylsulphone*, the corresponding iodo-compounds, and also moniodopropylorthotolylsulphone are all oils. Paratolylpropyleneglycol, $C_6H_4Me{\cdot}SO_2{\cdot}C_3H_5(OH)_2$, 93—95°. *α-Naphthyl compound*, $C_{10}H_7{\cdot}SO_2{\cdot}C_3H_5O$, 127°.

Benzylsulphamic Acid and Derivatives of Benzylsulphonitrosamic Acid. By CARL PAAL and LEOPOLD LOWITSCH (*Ber.*, 1897, **30**, 869—879).—In former papers (Paal and Kretschmer, Abstr., 1894, i, 365; Paal and Jänicke, Abstr., 1896, i, 235), it was shown that primary aromatic amines and hydrazines combine with amidosulphonic acid with the formation of the ammonium salts of sulphamic and hydrazidosulphonic acids, and it was further stated that fatty amines do not react quite in the same way, isoamylamine, for instance, forming the amylamine compound of isoamylsulphamic acid, $C_5H_{11}{\cdot}NH{\cdot}SO_3H,NH_2{\cdot}C_5H_{11}$. It therefore seemed interesting to study the behaviour of aromatic amines of the type of benzylamine under similar conditions. On boiling benzylamine with excess of amidosulphonic acid in alcoholic solution, the *benzylamine amidosulphonate*, $NH_2{\cdot}SO_3H,NH_2{\cdot}C_7H_7$, is alone produced, and only on heating the mixture in a closed tube at 200° does rearrangement take place, with the formation of *benzylamine benzylsulphamate*,

$$CH_2Ph{\cdot}NH{\cdot}SO_3H,NH_2{\cdot}C_7H_7.$$

The former compound forms white, glistening leaflets melting at 121°, and the latter long prisms melting at 179°.

On hydrolysing this benzylamine compound by means of hydrochloric acid, the corresponding *benzylsulphamic acid*, $CH_2Ph{\cdot}NH{\cdot}SO_3H$, is produced as a well defined crystalline substance forming long, white needles melting with decomposition at 194°, the *barium* salt forms colourless, transparent plates free from water of crystallisation, and the *silver* salt white needles, stable in the light, and very soluble in water.

On treating benzylsulphamic acid with potassium nitrite, *potassium benzylsulphonitrosamate*, $C_7H_7{\cdot}N(NO){\cdot}SO_3K$, is produced, the corresponding compound being formed with sodium nitrite, and although the free acid does not seem capable of existence, yet these salts readily combine with the hydrochlorides of organic bases, with formation of the amine salts of benzylsulphonitrosamic acid, thus the *isoamylamine* salt forms fine, white leaflets, decomposing at ordinary temperatures; the *aniline* salt, white needles, exploding on touching; the *phenylhydrazine* compound slender, white needles, also very explosive; the *paratoluidine* salt, white needles, very soluble in alcohol, and explosive even in the moist condition; and the *α-naphthylamine* salt, faintly red leaflets, which explode violently on scratching with a sharp piece of glass.

In many respects, the salts of benzylsulphonitrosamic acid show a remarkable resemblance to the diazo-compounds, thus on boiling with water, nitrogen is eliminated and benzylic alcohol produced, with halogen acids the corresponding benzylic haloid is formed, whilst ethylic alcohol gives rise to benzylic ethylic ether.

The product formed when α-naphthylamine benzylsulphonitrosamate explodes is an azo-dye, namely, the hydrochloride of *benzyl-*

azo-α-benzylnaphthylamine, $CH_2Ph{\cdot}N_2{\cdot}C_{10}H_6{\cdot}NH{\cdot}C_7H_7,HCl$, a substance crystallising from its beautifully blue solutions in small, dark blue needles, melting and decomposing at 224°; the *base* crystallises from ether in red needles. J. F. T.

Derivatives of Paratolylsulphnitrosamic Acid. By CARL PAAL and S. DEYBECK (*Ber.*, 1897, **30**, 880—887. Compare preceding abstract).—*Paratolylsulphamic acid*, on treatment with sodium nitrite, yields sodium *paratolylsulphonitrosamate*, $C_6H_4Me{\cdot}N(NO){\cdot}SO_3Na$, a white, crystalline salt decomposing on heating, and similar in its behaviour to the sodium benzyl-sulphonitrosamate previously described, yielding, as it does, with water, paracresol; with ethylic alcohol, paratolyl ethyl ether, and with hydrogen iodide, paraiodotoluene. With β-naphthol, it yields *paratolyl β-naphthyl ether*, $C_6H_4Me{\cdot}O{\cdot}C_{10}H_7$, a red compound crystallising from dilute alcohol in needles melting at 135°, and with α-naphthylamine hydrochloride, *paratolylazo-α-naphthylamine*, $C_6H_4Me{\cdot}N{:}N{\cdot}C_{10}H_6{\cdot}NH_2$, the *hydrochloride* of which crystallises from dilute alcohol containing hydrogen chloride, in blue black needles melting at 162—164°.

In the action of nitro-sulphuric acid on potassium paratolylnitrosamate, potassium *paratolylsulphonitramate*, $C_6H_4MeN(NO_2){\cdot}SO_3K$, is formed as the chief product. J. F. T.

Metatoluenesulphonic Acid. By JOHN J. GRIFFIN (*Amer. Chem. J.*, 1897, **19**, 183—199).—An historical sketch of the work done on the isomeric toluenesulphonic acids is given. To prepare metatoluenesulphonic acid, metatoluenesulphonamide is heated with hydrochloric acid in sealed tubes at 140° for 6 hours, cooled, and the ammonium chloride which separates filtered off; the solution is boiled with potassium hydroxide until there is no longer any odour of ammonia, the solution evaporated to dryness, and extracted with alcohol, when the potassium salt of metatoluenesulphonic acid is obtained in minute scales. When treated with phosphorus pentachloride, the latter yields the sulphonic chloride, and this by treatment with water gives the free acid, which remains liquid at a temperature of −18°. The *barium, lead, calcium, sodium, potassium, silver, magnesium, manganese, zinc,* and *copper* salts are described.

Metatoluenesulphonanilide, formed from aniline and metatoluenesulphonic chloride, crystallises from alcohol in large, monoclinic prisms, and from ether in small, prismatic crystals, melting at 72°.

Metatoluenesulphonorthotoluidide is formed from the sulphonic chloride and orthotoluidine; it crystallises in prisms and thick plates, melts at 108°, and is insoluble in water but readily soluble in ether, alcohol, and benzene.

Metatoluenesulphonparatoluidide prepared in a similar manner crystallises in small prisms, and melts at 106°. A. W. C.

Action of Ethylic and Methylic Alcohols on Paradiazometatoluenesulphonic Acid in the presence of Various Substances. By JOHN J. GRIFFIN (*Amer. Chem. J.*, 1897, **19**, 163—183).—Paradiazometatoluenesulphonic acid, prepared by diazotising para-

toluidinemetasulphonic acid, was submitted to the action of alcohol in presence of various substances, in order to determine whether the diazo-group is replaced by hydrogen or an ethoxy-group.

When the diazo-compound is acted on by methylic alcohol in presence of sodium methoxide, a hard, pale brown substance is produced, which, on treatment with phosphorus pentachloride and ammonia, is converted into metatoluenesulphonamide.

The same result is obtained if the sodium methoxide is replaced by sodium carbonate, sodium hydroxide, or zinc dust, or when ethylic alcohol is used instead of methylic alcohol. In the latter case, the yield of the amide is smaller. With methylic alcohol and calcium carbonate, no reaction takes place.

The product of the action of methylic alcohol and ammonia on the diazo-compound is the ammonium salt of paratoluidinemetasulphonic acid, which was proved by diazotising, decomposing with methylic alcohol and caustic soda, and treating the resulting substance with phosphorus pentachloride and ammonia, when metatoluenesulphonamide was again produced.

The best yield of the amide is obtained by treating the product obtained by the action of methylic alcohol and zinc dust in the diazo-compound with phosphorus trichloride (instead of the pentachloride) and ammonia.

Metatoluenesulphonamide melts at 108°, crystallises from water in brilliant hexagonal scales or large, fern-like growths, according to the concentration of the solution, and from alcohol in monoclinic prisms.

Metasulphaminebenzoic acid is produced when metatoluenesulphonamide is oxidised with sulphuric acid and potassium dichromate. It melts at 223° (uncorr.), and volatilises on gentle heating. When heated at 245—250° for 45 minutes and then cooled, it sets to a brown, vitreous mass, easily soluble in cold water, from which it crystallises in needles on evaporation.

Barium and silver salts of the acid are described. The latter contains no water of crystallisation, which is contrary to what has been previously stated to be the case. A. W. C.

Condensation of Hydrols with Aromatic Amines in Presence of Sulphuric Acid. By MAURICE PRUD'HOMME (*Bull. Soc. Chim.*, 1897, [iii], **15**, 717—720).—Nölting has shown that when aromatic amines, such as paratoluidine, condense with tetramethyldiamidobenzhydrol in presence of strong sulphuric acid, the leuco-bases of blue-green dyes are produced. In presence of hydrochloric acid, the products are leuco-bases of pure green dyes, replacement in the paratoluidine molecule taking place respectively in the ortho- and metapositions with regard to the amido-group.

The author compares the condensation of other benzhydrol derivatives with aromatic bases; he concludes that in sulphuric acid solution replacement in the amine takes place chiefly in the para-position, if the para-position is free, with the formation of violet-blue dyes. Replacement may, at the same time, take place in the ortho- or para-position, with formation of green dyes. M. W. T.

Benzyl Derivatives of Pararosaniline. By MAURICE PRUD'HOMME (*Bull. Soc. Chim.*, 1897, [iii], **15**, 720—723).—The author

has prepared a large number of the benzene derivatives of pararosaniline; he finds that the change of colour produced by the entry of a benzyl group into the molecule is practically equivalent to that produced by the introduction of a methyl group, the phenyl group having little influence when attached to a side chain. M. W. T.

Action of Acid Chlorides on Methoxynaphthol in presence of Aluminium Chloride. By L. ROUSSET (*Bull. Soc. Chim.*, 1896, [iii], **15**, 633—638).—A solution containing butyric chloride and α-methoxynaphthalene in molecular proportion is added, in small quantities at a time, to a flask containing aluminium chloride and carbon bisulphide, hydrogen chloride is given off, and a mixture of three isomeric *α-methoxynaphthyl propyl ketones* is obtained. By recrystallisation from alcohol, a compound, which probably corresponds with the formula $OMe\cdot C_{10}H_6\cdot COPr$ [= 1 : 4] is separated. This appears to be the chief product of the reaction; it melts at 49—50°, and forms a red, crystalline picrate which melts at 90° (compare this vol., i, 75). From the mother liquor, by the picric acid method already described, two isomeric ketones can be separated; one, a liquid, boils at 212—217° under 18 mm. pressure, and does not form a crystalline picrate; the other, a crystalline solid, melts at 33—34°, and forms a picrate which melts at 103—104°. By the action of acetic chloride on β-methoxynaphthalene, a large quantity of a ketone, $OMe\cdot C_{10}H_6\cdot COMe$, is obtained; this melts at 57°, boils at 205° under 22 mm. pressure, and is identical with the compound described by Gattermann. From the mother liquor, a small quantity of a liquid isomeride is obtained. M. W. T.

Conversion of Nitro-β-naphthaquinone into Indene Derivatives. By E. C. THEODOR ZINCKE (*Annalen*, 1897, **295**, 1—6. Compare Abstr., 1892, 1229).—Orthodichloronitroethylbenzoylcarboxylic acid, obtained by the action of chlorine on nitro-β-naphthaquinone, is converted by acetic chloride into an acetyl derivative which is devoid of acidic properties, and yields a dirty, flocculent substance when treated with warm, dilute soda (*loc. cit.*); nitrous acid is produced in the change, although no trace of this substance is eliminated when the original compound is treated with hot alkali. If the action of alkali on the acetyl derivative is conducted at the ordinary temperature, nitrous and acetic acids are produced, along with dichlorindenehydroxycarboxylic acid, $CCl{<}{\substack{C_6H_4\\ CCl-}}{>}C(OH)\cdot COOH$, which is recognised by oxidising it to dichlorindone.

The author explains this change by regarding dichloronitroethylbenzoylcarboxylic acid as acting towards acetic chloride in conformity with the structure $COOH\cdot CO\cdot C_6H_4\cdot CHCl\cdot CCl{:}NO\cdot OH$, giving rise to the unstable additive compound,

$$COOH\cdot CO\cdot C_6H_4\cdot CHCl\cdot CCl_2\cdot NAcO\cdot OH,$$

which loses the elements of hydrogen chloride, yielding the lactonic compound $C_6H_4{<}{\substack{CO\cdot CO\cdot O\\ CHCl-CCl\cdot NAcO\cdot OH}}$; rupture of the lactone ring, followed by elimination of water, and hydrolysis, leads to the substance $COOH\cdot CO\cdot C_6H_4\cdot CCl{:}CHCl$, which then passes into the indene derivative.

Orthochloronitromethoxyethylbenzoylcarboxylic acid also indifferent acetyl derivative (Abstr., 1894, i, 297); alkalis, however, do not eliminate nitrous acid from this substance, but merely regenerate the carboxylic acid. M. O. F.

Action of Chlorine on Amido-β-naphthaquinol: Dichlorotriketohydronaphthalene, Naphthapyrogallol, and other Products of Change. By E. C. THEODOR ZINCKE and HEINRICH NOACK (*Annalen*, 1897, **295**, 7—27).—Amido-β-naphthaquinol was first obtained by Groves (Trans., 1884, **45**, 299) on reducing 3-nitro-1 : 2-dihydroxynaphthalene with tin and hydrochloric acid, the nitro-derivative being prepared by the reduction of nitro-β-naphthaquinone with stannous chloride; the hydrochloride forms silvery, lustrous leaflets, and does not change when exposed to air. The *base* crystallises in small, lustrous needles, and melts at 164°, previously darkening and decomposing; it dissolves readily in alcohol and acetone, but is very sparingly soluble in ether and benzene. The compound dissolves in alkalis and alkali carbonates, forming yellow solutions, which rapidly become brown on exposure to air, and deposit highly coloured, insoluble substances; ferric chloride gives rise to a bluish-black precipitate, and sodium nitrite converts the base or its hydrochloride into a red substance which rapidly decomposes and evolves gas. The *diacetyl* derivative separates from acetone in long, lustrous needles, and melts and decomposes at 195°; the *triacetyl* derivative crystallises from glacial acetic acid in white, lustrous needles, and decomposes above 200°.

4-*Dichloro*-1 : 2 : 3-*triketohydronaphthalene*, obtained by passing a rapid stream of chlorine into amido-β-naphthaquinol suspended in concentrated hydrochloric and glacial acetic acids, crystallises from nitric acid (sp. gr. = 1·4) in small, lustrous prisms containing $2H_2O$; it melts and decomposes at 99°, and undergoes change when boiled with alcohol. The ketone does not dissolve in sodium carbonate, which colours it red, but caustic soda forms a violet solution which yields a reddish precipitate when acidified; bleaching powder oxidises the substance to phthalic acid, phenylenediamine gives rise to an azine, and sulphuric acid converts the ketone into isonaphthazarin.

1 : 2 : 3-*Trihydroxynaphthalene* (*naphthapyrogallol*), formed from the triketochloride by reduction with stannous chloride, crystallises in lustrous prisms on adding hydrochloric acid to its solution in absolute alcohol; it becomes dark and decomposes above 250°, and rapidly decomposes when the aqueous solution is heated. The substance dissolves readily in acetone and alcohol, but with difficulty in glacial acetic acid, the solutions undergoing rapid change when heated; it dissolves in alkalis and alkali carbonates, forming almost colourless solutions which rapidly become reddish, and finally dark red. The *triacetyl* derivative crystallises from glacial acetic acid in colourless prisms or plates, and melts to a red liquid at 250—255°; nitric acid oxidises this compound to a substance which crystallises from benzene in small, reddish-yellow needles.

4-*Dichloro-3-ketonaphthaphenazine*, $\begin{array}{l}CCl_2\cdot C_6H_4\cdot C{:}N\\ | \qquad\qquad\quad\;\; |\\ CO\text{———}C{:}N\end{array}\!\!>C_6H_4$, which is obtained on adding a solution of orthophenylenediamine in glacial acetic

acid to dichlorotriketohydronaphthalene dissolved in the same medium, crystallises in beautiful, lemon yellow needles, melting and darkening at 196—197°; it dissolves with difficulty in hot alcohol and glacial acetic acid, undergoing decomposition if left for long in contact with the solvents. Concentrated sulphuric acid forms a red solution, and hot alcoholic potash develops a deep green coloration, a dark violet precipitate being formed on treatment with glacial acetic acid.

3 : 4-*Hydroxychloronaphthaphenazine* (*α-chloronaphtheurhodole*),

$$\begin{matrix} CCl\cdot C_6H_4\cdot C{:}N \\ \| \qquad\qquad\quad | \\ C(OH)\text{——}C{:}N \end{matrix}\!\!>C_6H_4,$$

prepared by reducing the foregoing naphthaphenazine in alcoholic solution with stannous chloride, crystallises from glacial acetic acid in long, lemon yellow needles melting at 199—200°; the *sodium* derivative crystallises in deep red needles, and the *hydrochloride* and *nitrate* are also red, and exhibit metallic lustre. Oxidation with nitric acid converts the eurhodole into diketonaphthaphenazine (Abstr., 1895, i, 615).

3 : 4-*Diamido*-1 : 2-*dihydroxynaphthalene* is obtained by adding diazobenzene chloride to an acidic solution of amido-β-naphthaquinol hydrochloride and reducing the azo-compound with stannous chloride; it is rapidly oxidised in air, and develops a bluish-violet coloration with sodium carbonate. The *hydrochloride* crystallises in small, lustrous needles, and dissolves very readily in water; the aqueous solution darkens on standing, but is stable in presence of free hydrochloric acid.

Azimido-β-naphthaquinone, $\begin{matrix} CO\text{———}C\text{—}N \\ | \qquad\qquad\quad \| \\ CO\cdot C_6H_4\cdot C\cdot NH \end{matrix}\!\!>N$, is obtained by the action of nitrous or nitric acid on the hydrochloride of diamidodihydroxynaphthalene, and crystallises from a mixture of nitric and glacial acetic acids in small, orange-red plates, darkening above 220°; the solution in caustic soda is colourless, whilst sodium carbonate develops a brownish-red coloration. When reduced with stannous chloride, the substance yields *azimidonaphthaquinol*, which crystallises in lustrous, almost colourless, needles; the *hydrochloride* crystallises in beautiful, red needles from alcohol containing hydrochloric acid.

Azimidonaphthaphenazine, $C_6H_4<\begin{matrix} N{:}C\cdot C_6H_4\cdot C\cdot NH \\ \quad | \qquad\qquad \| \\ N{:}C\text{———}C\text{—}N \end{matrix}\!\!>N$, is produced by the action of orthophenylenediamine on azimido-β-naphthaquinone, and crystallises from hot glacial acetic acid in small, bright yellow needles, undergoing no change at 250°; it is insoluble in alkalis, and forms yellow salts with acids. M. O. F.

Action of Ethylic Oxalate on Aromatic Amines. III and IV. By RICHARD E. MEYER and WILHELM MÜLLER (*Ber.*, 1897, **30**, 770—774 and 775—779).—Ethylic oxalate condenses with amines of the naphthalene series, forming compounds analogous to those produced with amines of the benzene series.

With α-naphthylamine in the absence of alcohol, besides the ethylic α-naphthyloxamate already prepared by Ballo, *α-dinaphthyloxamide*, $C_{10}H_7\cdot NH\cdot CO\cdot CO\cdot NH\cdot C_{10}H_7$, is produced; the latter crystallises from

glacial acetic acid in slender needles melting at 234°. With β-naphthylamine, *ethylic β-naphthyloxamate*, $C_{10}H_7\cdot NH\cdot CO\cdot CO\cdot OEt$, and *$\beta$-dinaphthyloxamide* are formed, the latter crystallising from glacial acetic acid in colourless needles melting at 276°, and the former separating from boiling alcohol in colourless leaflets melting at 119·5°, *β-naphthyloxamic acid*, $C_{10}H_7\cdot NH\cdot CO\cdot COOH$, prepared from the above ethylic salt by hydrolysis with potash, forms white, glistening needles melting with effervescence at 190°. *β-Naphthyloxamide*,

$$C_{10}H_7\cdot NH\cdot CO\cdot CONH_2,$$

obtained by the action of ammonia on the acid, crystallises from alcohol in colourless leaflets melting at 248°.

With 1 : 2-naphthylenediamine, ethylic oxalate produces *1 : 2-naphthylenoxamide*, $C_{10}H_6<\begin{matrix}NH\cdot CO\\ | \\ NH\cdot CO\end{matrix}$, which crystallises from glacial acetic acid in small, yellow needles, and does not melt below 300°, whilst with 1 : 4-naphthylenediamine ethylic *1 : 4-naphthylenedioxamate*,

$$C_{10}H_6(NH\cdot CO\cdot COOEt)_2,$$

is formed, the reaction proceeding similarly to the condensation of ethylic oxalate with paraphenylenediamine; it separates from alcohol in colourless, glistening needles melting at 203°. *1 : 4-Naphthylenedioxamide* is an insoluble substance which does not melt at 300°; 1 : 4′-naphthylenediamine and oxalic ether, in like manner, yield *ethylic 1 : 4′-naphthylenedioxamate*, crystallising from alcohol in colourless needles melting at 206—208°, the corresponding *acid* melting at 235°; *1 : 4′-naphthylenedioxamide* crystallises from boiling alcohol in slender needles and does not melt at 300°.

1 : 1′-Naphthylenediamine reacts with ethylic oxalate somewhat differently from its isomerides, the red compound of de Aguiar being produced. For this substance, the authors propose the formula

$$C_{10}H_6<\begin{matrix}NH\cdot CO\\ \quad | \\ N = C\cdot OEt\end{matrix}.$$

J. F. T.

Constitution of Cymene and of the Terpene in Cummin Oil (Cuminum cyminum). By L. J. WOLPIAN (*Chem. Centr.*, 1896, i, 920—921, 1067; from *Pharm. Zeit. Russ.*, **35**, 97—101, 145—149).—The oil of cummin used by the author had a specific gravity = 0·892 at 18°, and a rotatory power of + 7° 23′ in a 100 mm. tube. The portion distilling below 220° was treated with sodium hydrogen sulphite solution and fused potassium hydroxide, then boiled with metallic sodium and again distilled. The clear, strongly refractive liquid thus obtained had the odour of eucalyptus oil, and consisted of cymene and terpene, which cannot, however, be completely separated by fractionation. The fraction distilling at 160—169° showed a rotation of about + 20°, that at 169—176° of about + 8°. From the latter, which is rich in cymene, the terpene (pinene?) was isolated by conversion into the hydrochloride, which boils at 208°, by passing in dry hydrogen chloride at − 18°, then shaking the saturated solution with water and sodium carbonate solution, drying, and finally fractionating under 40 mm. pressure with a Löbel's dephlegmator. The largest fraction, boiling at 103—106°, showed a rotation of + 1° 17′ and was again submitted to the same treatment. In this way, pure

cymene boiling at 173·5—174·5° under 763 mm. pressure, of sp. gr. = 0·8588 at 20° and 0·8595 at 15° and of refractive index 1·479, was obtained. It was further identified as methylisopropylbenzene by conversion into the barium salts of α- and β-sulphocumic acids (Klaus), by preparation of the sodium salt of α-sulphocumic acid (from the α-barium salt) and of the α-sulphonamide melting at 115—116°. The α-sulphonamide of normal methylpropylbenzene melts at 101—102°.

From a comparison with cymene from cummin, the author regards all cymenes found in ethereal oils and obtained from terpenes as being the isopropyl compound. Attempts to convert cymene into terpene gave unsatisfactory results. The portions distilling below 170° obtained from the purified mixture of cymene and terpene, after repeated fractionation over sodium, gave a terpene of boiling point 157—158° at 768 mm. pressure, of sp. gr. = 0·8604 at 20°, and specific rotatory power $[\alpha]_D = +29·46$. By passing hydrogen chloride into a solution of this terpene in carbon bisulphide, an optically inactive liquid hydrochloride was obtained, of which the greater portion boils at 142—158° under 50 mm. pressure, and has a sp. gr. = 0·94 at 16°. A liquid bromide, $C_{10}H_{16}Br_2$, easily soluble in alcohol, ether, and chloroform, of sp. gr. = 1·1243 at 18°, and specific rotatory power $[\alpha]_D = +7·04$ was prepared by bromination in acetic acid solution. The author was unable to obtain a crystalline nitrosyl chloride compound of hydrocumene by Wallach's method, and believes that this incapacity of the terpene of oil of cummin to form crystalline compounds shows it to be different from the terpenes hitherto examined. This terpene is very similar to Flawitzky's terpene prepared from Russian turpentine oil.

E. W. W.

The Chemical and Industrial Importance of Ethereal Oils. Cinnamon Oils. By DUYK (*Chem. Centr.*, 1896, ii, 358; from *J. Pharm. d'Anvers*, 1896, April).—Whilst the German, American, and Swiss pharmacopœias prescribe the oil of *Cinnamomum cassia*, in Belgium the oil from the bark of *C. zeylanica* is officinal. The latter has a density of 1·024, contains about 60 per cent. of cinnamaldehyde, and is optically inactive. Its alcoholic solution is said to give with ferric chloride a pale green, and not the bluish-green coloration indicative of eugenol. The oil contains 6—8 per cent. of eugenol, phellandrene, and small quantities of safrole, &c., whilst that from the leaves and roots of the same plant consists chiefly of eugenol and a solid "camphor." The Ceylon cinnamon oil is much adulterated. The inferior Cassia oil of density 1·055—1·065 contains 70—78 per cent. of cinnamaldehyde besides cinnamylic acetate, eugenol, a terpene, and methylorthocumaraldehyde. It is miscible with strong alcohol, and its alcoholic solution turns brown with ferric chloride. It is often adulterated with paraffin or colophony. A good oil, on distillation, should not leave a residue of more than 8—10 per cent.

E. W. W.

Action of Hydrogen Chloride on Licareol, Licarhodol, and Lemonol. By PHILIPPE BARBIER and LOUIS BOUVEAULT (*Bull. Soc. Chim.*, 1896, [iii], **15**, 594—597. Compare Abstr., 1893, i, 514).—When hydrogen chloride is passed into lemonol, obtained from the oil of

Andropogon Schœnanthus, it is readily absorbed, an oily product boiling at 120—125° (10 mm.), and having a sp. gr. = 1·0569 being obtained. The composition of this oil, which contains a little unaltered lemonol, is represented by the formula $C_{10}H_{18}Cl_2$. When heated with an acetic acid solution of fused potassium acetate and distilled, it yields two fractions, the first boiling at 170—180°, and consisting of a mixture of quadrivalent terpenes, whilst the second consists of the acetate of lemonol, $C_{10}H_{17}OAc$. The latter, on hydrolysis, gives pure inactive lemonol boiling at 114—116° (10 mm.). This reaction points to the existence in the oily hydrochloride of two isomeric substances, the one saturated, the other unsaturated; the former yielding the mixture of terpenes, the latter the acetate. The amount of bromine with which this oil is capable of uniting points to the existence in it of these two substances in nearly equal proportions. Licareol, saturated with hydrogen chloride, yields a product which can be easily converted into acetate of lemonol, and then into lemonol itself. Licarhodol, produced by isomeric change from licareol when the latter is heated with acetic anhydride, yields, on saturation with hydrogen chloride, the same mixture of hydrochlorides. The author insists that licareol and licarhodol are two distinct alcohols, rotating the plane of polarised light in opposite senses, but easily converted into the optically inactive alcohol, lemonol. A. C. C.

Researches on Camphor. By ENRICO RIMINI (*Gazzetta*, 1896, **26**, ii, 502—517).—An almost quantitative yield of fenchonoxime is obtained by cautiously heating a solution of pure fenchone (70 grams) in alcohol (300 c.c.) with hydroxylamine hydrochloride (50 grams) and stick soda (140 grams) on the water bath, and, after several hours' boiling, adding a similar quantity of hydroxylamine salt in two portions; the alcohol is partially distilled off, the residual solution precipitated by water, and the oxime recrystallised from light petroleum. Fenchonoxime melts at 165°, and is nearly insoluble in alkali. When its dilute hydrochloric acid solution is treated with sodium nitrite, a violent reaction occurs, and *pernitrosofenchone*, $C_{10}H_{16}N_2O_2$, is formed; it crystallises in transparent, white scales melting at 66—67°, and has an odour resembling that of the isomeric pernitrosocamphor. Like the latter, it probably contains the group $:CN_2O_2$. When heated with alcoholic potash, it yields fenchone, but if treated with cold alcoholic potash or ammonia it is converted into the isomeric *isopernitrosofenchone*, which crystallises in colourless, orthorhombic tablets [$a : b : c = 0·6775 : 1 : 0·4626$] melting at 88°; the reverse change could not be effected. Pernitrosofenchone is converted into fenchone by boiling with hydroxylamine hydrochloride in alkaline solution and into isocamphor (Angeli & Rimini, this vol., i, 88) by concentrated sulphuric acid; isocamphor is also obtained by treating isopernitrosofenchone with concentrated sulphuric acid.

Pernitrosomenthone, $C_{10}H_{18}N_2O_2$, is prepared by the action of sodium nitrite on menthonoxime dissolved in acetic acid; it is an oil which, when distilled under reduced pressure decomposes at 140°, and is converted into menthone by treatment with sulphuric acid or alkalis. Menthonoxime yields menthone when oxidised by alkaline potassium ferricyanide solution.

Camphoroxime is oxidised by potassium ferricyanide in cold soda solution, yielding a bright blue compound $(C_{10}H_{15}NO)_2$, which melts at 104—105°, and gives a blue solution in light petroleum; it has the normal molecular weight in freezing benzene, and probably has the constitution $\begin{matrix} CH_2 \\ | \\ C_8H_{14} \end{matrix}\!\!>\!C(NO)\cdot C(NO)\!<\!\!\begin{matrix} CH_2 \\ | \\ C_8H_{14} \end{matrix}$. This constitution is in accordance with its behaviour towards hydrochloric acid, which converts it into a mixture of camphoroxime and camphor. W. J. P.

Action of Nitrous Acid on Camphoroxime. By ANGELO ANGELI and ENRICO RIMINI. (*Gazzetta*, 1896, **26**, ii, 517—521).—The acid of the composition $C_8H_{14}O_4$, previously prepared by the authors (this vol., i, 89) by oxidising isocamphor, easily forms an anhydride, and yields succinic acid when oxidised with chromic acid; it may be synthesised by reducing diethylic isoproplyacetonedicarboxylate, and is identical with an α-isopropylglutaric acid prepared by W. H. Perkin, jun. (Trans., 1896, 1495). The identity of the authors' preparation with that of Perkin is established by a crystallographic examination of the anilides; they are orthorhombic [$a : b : c = 0{\cdot}9520 : 1 : 2{\cdot}7383$] and melt at about 160°.

It follows that isocamphor contains the group

$$\begin{matrix} CHMe_2\cdot CH\cdot CH_2\cdot CH_2\cdot C\equiv \\ | \qquad\qquad\qquad \\ C\equiv \qquad\qquad\qquad \end{matrix}$$

W. J. P.

Asafœtida. By J. POLÁSEK (*Arch. Pharm.*, 1897, **235**, 125—132). —Pure drops of *Asafœtida amygdaloides* gave the following results on analysis:—Resin soluble in ether = asaresinotannol ferulate, 61·40; resin insoluble in ether = free asaresinotannol, 0·60; gum, 25·1; ethereal oil, 6·7; vanillin, 0·06; ferulic acid, 1·28; moisture, 2·36 per cent. On hydrolysis with potassium carbonate, the soluble resin yields a resinotannol, named asaresinotannol by the author, and ferulic acid; on hydrolysis with sulphuric acid, however, it is decomposed into the same tannol and umbelliferone. The author has succeeded in obtaining umbelliferone by the action of sulphuric acid (55 per cent.) on a mixture of ferulic acid and resorcinol; guaiacol is formed at the same time. *Asaresinotannol*, $C_{24}H_{34}O_5$, is a brownish-yellow powder, readily soluble in alcohol, potash, acetone, chloroform, amylic alcohol, and acetic acid, sparingly so in ether, benzene, carbon bisulphide or ammonia, but insoluble in light petroleum. Since it yields a *monobenzoyl* and a *monacetyl* derivative, it contains a hydroxyl group. On oxidation with nitric acid, it yields picric acid. J. J. S.

Glucosides of Black and White Mustards. By J. GADAMER (*Arch. Pharm.*, 1897, **235**, 44—114. Compare this vol., i, 254).—The silver compound, $C_4H_5NAg_2S_2O_4 + H_2O$, obtained by the action of silver nitrate on an aqueous solution of sinigrin, is formed according to the equation $C_{10}H_{16}KNS_2O_9 + 2AgNO_3 + H_2O = C_4H_5NAg_2S_2O_4 + C_6H_{12}O_6 + KNO_3 + HNO_3$; this was proved by estimating the acidity and rotatory power of the resulting liquid. The silver compound is undoubtedly not a simple molecular compound of phenylthiocarbimide with normal silver sulphate, as it cannot be obtained by mixing these two compounds. Its behaviour with ammonia also speaks against this additive constitution.

Hydrochloric acid decomposes the compound, yielding silver chloride, free sulphur, sulphuric acid, and probably allylic cyanide; it is also decomposed when heated alone or with water, the products being phenylthiocarbimide, silver sulphide and sulphate, and carbon bisulphide. All these reactions indicate that the two atoms of silver are differently situated in the molecule. A similar *mercury* compound can be obtained by treating a solution of sinigrin with mercurous nitrate, or by the action of metallic mercury on the silver salt. When solutions of sinigrin and silver nitrate in the proportion of 3 mols. of the former to 4 of the latter are mixed, no precipitate is obtained, owing to the formation of a double compound, $C_4H_5SNAg_2SO_4 + C_4H_5SNAgKSO_4$.

A solution of sinigrin when added to barium chloride, yields no precipitate of barium sulphate in the cold, but complete decomposition ensues when the mixture is heated; barium hydroxide, on the other hand, yields a precipitate at once; in this respect, sinigrin resembles potassium ethylsulphate. The author has studied the action of ammonia on sinigrin both under pressure and in the cold, but no definite products could be isolated. An acetic acid solution of phenylhydrazine decomposes sinigrin and yields phenylglucosazone (m. p. 204°).

Sinalbin (compare Will and Laubenheimer, *Annalen*, **199**, 150, and this vol., i, 255) occurs in white mustard, but no trace of it can be found in black, and similarly no trace of sinigrin is to be found in white mustard. Sinalbin reacts with barium chloride or hydroxide in exactly the same manner as sinigrin.

Sinapin iodide, when anhydrous, melts at 178—179°, and forms a periodide when heated with alcoholic iodine solution at 100°. The crystalline bromide, $C_{16}H_{24}NO_5Br + 3H_2O$, melts at 90—92°, but the anhydrous salt at 107—115°. *Sinapin nitrate*, $C_{16}H_{24}NO_5 \cdot NO_3$, is readily soluble in water, but crystallises from alcohol with $2H_2O$.

Ethylic sinapate, $C_{11}H_{11}O_5Et + H_2O$, crystallises in colourless scales, melts at 80—81°, and is insoluble in water but readily dissolves in ether and alcohol; it loses its water of crystallisation when kept over sulphuric acid, and becomes soft. *Acetylsinapic acid* crystallises in needles and melts at 181—187° and not at 281° as stated by Remsen and Coale (Abstr., 1884, 1388); the author has proved that it is a monacetyl derivative by estimating the amount of acetic acid formed on hydrolysis. When heated with hydriodic acid, sinapic acid yields methylic iodide, the amount formed corresponding with two methoxy-groups in the original acid. *Methylic methylsinapate*, which crystallises in yellowish plates and melts at 91—91·5°, when hydrolysed, yields *methylsinapic acid*, melting at 123·5—124°. This acid, when oxidised with an alkaline solution of potassium permanganate, yields trimethylgallic acid, $C_6H_2(OMe)_3COOH$ [$COOH : (OMe)_3 = 1 : 3 : 4 : 5$.] No definite oxidation product could be obtained from sinapic acid.

J. J. S.

Constituents of the Root of Ononis Spinosa, L. By HERMANN THOMS (*Arch. Pharm.*, 1897, **235**, 28—39).—Ononin, a constituent of the root of *Ononis spinosa*, is usually contaminated with more or less of a wax-like substance, which Hlasiwetz (*J. pr. Chem.*, 1855, **65**, 419) termed onocerin. The author has prepared larger quantities

of the latter by extracting the root with 90 per cent. alcohol and then treating the extract with 60 per cent. alcohol in which onocerin is insoluble. It crystallises in minute prisms, melts at 232°, and is but sparingly soluble in the usual organic solvents; it dissolves more readily, however, in amylic alcohol, turpentine, or glacial acetic acid. If dissolved in concentrated sulphuric acid, it gives a yellow solution, and when sulphuric acid is poured into an acetic acid solution, a bluish-green band is formed at the junction of the two liquids, the acetic acid solution becoming red after a time. Onocerin has the composition $C_{26}H_{44}O_2$; it yields a *diacetyl* derivative melting at 224°, and probably a *dibenzoyl* derivative. Bromine reacts with an acetic acid solution of the acetyl compound, yielding a *tetrabromide*, $C_{26}H_{42}O_2Ac_2,Br_4$ or $C_{26}H_{38}Br_4O_2Ac_2$. When oxidised with chromic mixture, onocerin is converted into a diketone, *onoketone*, $C_{26}H_{40}O_2$, which melts at 186—187°. The *hydrazone*, $C_{26}H_{40}(N{\cdot}NHPh)_2$, *ketoxime*; $C_{26}H_{40}(NOH)_2$, and *semicarbazone*, $C_{26}H_{40}ON{\cdot}NH{\cdot}CO{\cdot}NH_2$, are described. Onoketone, when further oxidised with chromic mixture, yields acetic and butyric acids, together with an *acid*, $C_{20}H_{38}O_2$, which melts at 73—74°, and a resinous *acid*, $C_{20}H_{35}O_5$. It is probable that other products are also formed.

The author suggests the name *onocol* instead of onocerin for the original compound, since it is undoubtedly a secondary alcohol. J. J. S.

Phytosterin. By HERMANN THOMS (*Arch. Pharm.*, 1897, **235**, 39—43).—The term phytosterin was first introduced by Hesse (*Annalen*, 1878, **192**, 175) for vegetable cholesterol. Other investigators have shown that, not only is vegetable cholesterol different from animal cholesterol, but also that the former differs in certain of its physical properties according to the source from which it is obtained. The author points out that other substances of vegetable origin, for example, cynanchol (*Annalen*, 1878, **192**, 152), quebrachol (*ibid.*, 1882, **211**, 272), cupreol (*ibid.*, 1885, **228**, 288, and 1886, **234**, 375), cinchol, lactucerol (*ibid.*, **234**, 243), urson (*Monatsheft.*, 1893, **14**, 255), amyrin (*Ber.*, 1887, **20**, 1242, and 1891, **24**, 3836), and lupeol (*ibid.*, 1891, **24**, 2709), give not only Liebermann's colour reaction (*Ber.*, 1885, **18**, 1804), but also Hesse's reaction for cholesterol. Other substances, such as onocol, onoketone (see preceding abstract), benzoresinol (*Arch. Pharm.*, 1893, **233**, 209), and abietic acid also give the same reactions. It is obvious that these characteristic cholesterol reactions do not simply depend on the alcoholic character of the substances, since certain resinous acids also give them. The author suggests that the term phytosterin should be given to all unsaturated alcohols of high molecular weight which give the characteristic cholesterol colour reactions, and which owe their origin to physiological processes similar to those which produce cholesterol. J. J. S.

Compounds from Lichens. By WILHELM ZOPF (*Annalen*, 1897, **295**, 222–256. Compare this vol., i, 255).—The sources and properties of atranoric acid, $C_{19}H_{18}O_8$, and hæmatommic acid, $C_{11}H_{12}O_5$, obtained from it by the action of absolute alcohol at 150°, have been already indicated (*loc. cit.*). *Atranorinic acid* is produced when atranoric acid

is heated with water in sealed tubes at 150°, and crystallises in colourless needles; it melts at about 101°, dissolves somewhat readily in hot water, and forms a yellow solution in alkalis. *Atraric acid* is also obtained from atranoric acid by the action of water, and crystallises in thin, micaceous leaflets; it melts at about 140—141°, dissolves sparingly in hot water, and does not form yellow solutions with alkalis.

Psoromic acid (compare Abstr., 1895, i, 298) crystallises in small, snow-white needles, and melts to a dark brown liquid at 263–265°; it dissolves freely in acetone, but only very sparingly in cold ether, chloroform, and alcohol, these solvents dissolving it more readily when heated. It is scarcely soluble in benzene, and cold alkali carbonates dissolve it with difficulty, whilst caustic alkalis form yellow or reddish-yellow solutions; a dilute alcoholic solution develops a deep red coloration with ferric chloride. The alkali salts are very characteristic, crystallising in rosettes of dark red needles, and being readily soluble in water, must be precipitated from solution by treatment with carbonic anhydride; the barium and calcium salts are reddish-brown and do not dissolve in water.

Usnic acid (compare Abstr., 1895, i, 298; 1896, i, 104; also this vol., i, 256) crystallises in yellowish-green prisms, melts at 195—197°, and decomposes above 200°, yielding a carbonaceous residue; it is very sparingly soluble in hot alcohol, ether, and light petroleum, but dissolves freely in hot chloroform and benzene. It dissolves with difficulty in aqueous ammonia, more readily in caustic alkalis and solutions of the alkaline earths, with development of a yellow coloration, which becomes brown on heating the liquid; ferric chloride develops a brownish-red coloration with an alcoholic solution of the substance. Usnic acid is most conveniently identified by converting it into decarbusnein, which is obtained by heating the acid with absolute alcohol in sealed tubes at 150°; this crystallises from dilute alcohol in slender, colourless needles, and melts at 175°.

Stereocaulic acid (Abstr., 1896, i, 104) is obtained in quantity amounting to about 0·7 per cent. from *Stereocaulon alpinum*, collected on the Col di Rodella, in the Dolomites; it crystallises from alcohol in hemispherical aggregates of minute, lustrous prisms, has the empirical formula $C_9H_{10}O_3$, and melts at 193—195° (compare *loc. cit.*). The alcoholic solution reddens litmus, and develops a beautiful violet coloration with ferric chloride; the substance is insoluble in light petroleum, dissolves with great difficulty in cold alcohol, ether, benzene, and chloroform, freely, however, in boiling alcohol and glacial acetic acid. The *acetyl* derivative is obtained by the action of acetic anhydride, and crystallises from absolute alcohol in aggregates of minute needles melting at 186—187°; hydrolysis with dilute potash regenerates stereocaulic acid, along with a certain amount of orcin.

Salazinic acid, extracted by chloroform from *Stereocaulon salazinum* (Bory), is a microcrystalline powder which darkens at 235° and becomes blackish-brown at 250° without undergoing fusion; it dissolves in hot alcohol, ether, chloroform, and glacial acetic acid with difficulty, and is insoluble in boiling benzene. Alkali carbonates yield yellow solutions which darken when heated, and after some time deposit the alkali salts in minute, red needles which resemble the salts

of psoromic acid. *Stereocaulon denudatum* (Flörke), *var. pulvinatum* (Schaerer), which is identical with *var. compactum* (Körber), contains atranoric and psoromic acids.

Catocarpus alpicolus (Wahlbg.), or *Catocarpon chionophilum* (Fries) closely resembles *Rhizocarpon geographicum* morphologically, and has been classified by Körber as *var. alpicolum* of that group; it is now found that the resemblance extends to the composition of the lichens, which both contain psoromic and rhizocarpic acids. The latter substance is also present in *Biatora lucida* (compare Abstr., 1895, i, 298), which does not, as stated by Knop, contain usnic acid; *Rhizocarpon geographicum* is also destitute of usnic acid.

An analogous chemical resemblance has been traced between *Candelaria concolor* (Dickson), which is identical with *Xanthoria concolor* (Fries), *Candelaria vulgaris* (Massalongo), and *Lecanora laciniosa* (Duf. and Nylander), and the two closely allied lichens, *Callopisma vitellinum* (Ehrhardt) and *Physcia medians* (Nylander); all three contain calycin and callopismic (ethylpulvic) acid.

It has been shown (Abstr., 1896, i, 103) that *Physcia cæsia* (Hoffmann) or *Parmelia cæsia* (Acharius), when collected in sandy districts, contains atranoric and hæmatommic acids, along with zeorin; this is also the case when the lichen is dolomitic. *Placodium crassum* (Hudson), from this source, also resembles that obtained from North Germany, both specimens being destitute of psoromic acid, and giving indications of the presence of usnic acid; Spica, however (Abstr., 1883, 80), states that both acids are present in Sicilian *Placodium*. *Placodium Lagascæ* (Ach.), a rare chalk lichen occurring in the Dolomites, contains psoromic and usnic acids, along with a substance which has not been further investigated; it is destitute of atranoric acid, hæmatommic acid, and zeorin.

An instance of two varieties, or morphologically allied forms, differing from one another chemically, is afforded by *Placodium melanaspis, var. stellata* (Fries), and *P. m. var. alphoplaca* (Wahlenberg); as already stated (*loc. cit.*), the former contains atranoric acid and placodin, but it is now found that the *var. alphoplaca* contains psoromic acid along with a compound which, although red, is not identical with placodin.

Hæmatomma ventosum (Laurer, Schaerer) contains usnic acid and *ventosaric acid*, which crystallises in colourless prisms and melts at 205—207°; caustic soda develops a yellow coloration, which gradually becomes purple, and finally violet.

Lecanora thiodes (Sprengel) contains atranoric acid and zeorin.

M. O. F.

Action of Phosphorus Pentachloride on Imides of Dibasic Acids. By RICHARD ANSCHÜTZ (*Annalen*, 1897, **295**, 27—28).—Introductory to the following abstracts. M. O. F.

Action of Phosphorus Pentachloride on Succinanil and Dichloromaleinanil. By RICHARD ANSCHÜTZ and CHARLES BEAVIS (*Annalen*, 1897, **295**, 29—43. Compare Abstr., 1895, i, 176).—It has been shown that phosphorus pentachloride converts succinanil into tetrachloro-1-phenylpyrolline and dichloromaleinanil dichloride (*loc. cit.*); the latter substance is also formed when the chloride acts on

dichloromaleinanil, the main product, however, consisting of *tetrachlorosuccinanil*, $NPh<\begin{matrix}CO\cdot CCl_2\\ | \\ CO\cdot CCl_2\end{matrix}$, which crystallises from methylic alcohol and melts at 157—158°.

Dichloromaleindianil, $NPh<\begin{matrix}CO\text{——}CCl\\ \quad\quad || \\ C(NPh)\cdot CCl\end{matrix}$, is obtained by adding aniline dissolved in chloroform to dichloromaleinanil dichloride in the same medium, and crystallises from acetone in yellow cubes melting at 186—187°.

Anilidochloromaleinanil, $NPh<\begin{matrix}CO\cdot C\cdot NHPh\\ || \\ CO\cdot CCl\end{matrix}$, is produced on heating dichloromaleinanil with aniline and a small quantity of chloroform in closed tubes at 100°; it crystallises from alcohol or acetone in yellow, prismatic needles, and melts at 188—189°.

Methylanilidochloromaleinanil, $NPh<\begin{matrix}CO\cdot C\cdot NMePh\\ || \\ CO\cdot CCl\end{matrix}$, is obtained by heating dichloromaleinanil dichloride with methylaniline and chloroform in sealed tubes at 100°, and separates from acetone in small, yellowish-brown crystals melting at 188—189°; it is also formed when dichloromaleinanil and methylaniline are heated in chloroform at 100°.

Reduction of dichloromaleinanil dichloride with sodium amalgam leads to the formation of γ-anilidobutyrolactam (*loc. cit.*), and when this is hydrolysed and treated with silver nitrate, *silver* γ-anilidobutyrate is obtained; the *hydrochloride* of γ-anilidobutyric acid melts at 135·5—136·5°.
M. O. F.

Action of Phosphorus Pentachloride on Succinoparatolil.

By Richard Anschütz and Alfred Guenther (*Annalen*, 1897, **295**, 43—55).—*Dichloromaleinparatolil dichloride*, $C_6H_4Me\cdot N<\begin{matrix}CO-CCl\\ || \\ CCl_2\cdot CCl\end{matrix}$, is obtained by heating succinoparatolil with phosphorus pentachloride in a reflux apparatus at 80° and subsequently at 120°, and after crystallisation from benzene, melts at 156°; the crystals belong to the monosymmetric system; $a:b:c = 0·4422:1:0·4680$, and $\beta = 83°\ 3'$. The *compound*, $C_{11}H_{10}Cl_4NPO_2$, occurs as a bye-product, and separates from hot acetone in white crystals melting at 237°.

Dichloromaleinparatolil, $C_6H_4Me\cdot N<\begin{matrix}CO\cdot CCl\\ || \\ CO\cdot CCl\end{matrix}$, is obtained by treating the dichloride with boiling water, or boiling dilute alcohol; it crystallises from alcohol in long, silky needles, and melts at 193°.

Anilidochloromaleinparatolil, $C_6H_4Me\cdot N<\begin{matrix}CO\cdot C\cdot NHPh\\ || \\ CO\cdot CCl\end{matrix}$, is produced when dichloromaleinparatolil is heated with aniline and chloroform in a sealed tube, and crystallises from acetone in yellow scales melting at 40°; *piperidochloromaleinparatolil* crystallises from acetone in yellow scales, and melts at 130°.

Dichloromaleinparatolil dimethyl ether, $C_6H_4Me\cdot N<\begin{matrix}CO\text{——}CCl\\ \quad\quad || \\ C(OMe)_2\cdot CCl\end{matrix}$, is

formed on adding dichloromaleintolil dichloride to hot, absolute methylic alcohol, and melts at 98°; the *diethyl ether*, which melts at 88°, belongs to the monosymmetric system; $a:b:c = 0·3888:1:0·3945$; $\beta = 78° 9'$.

Dichloromaleinparatolilanil, $C_6H_4Me·N\Big\langle\begin{matrix}CO\text{———}CCl\\ \quad\quad\quad\ \ \|\\ C(NPh)·CCl\end{matrix}$, is obtained on allowing a mixture of dichloromaleintolil dichloride and aniline dissolved in chloroform to stand for some days; it crystallises from alcohol or acetone in scales or prismatic needles, and melts at 141°; *dichloromaleindiparatolil* crystallises from acetone in yellow needles, and melts at 161°.

Dichloromaleinparatolildipiperidide, $C_6H_4Me·N\Big\langle\begin{matrix}CO\text{————}CCl\\ \quad\quad\quad\quad\ \ \|\\ C(NC_5H_{10})_2·CCl\end{matrix}$, is obtained by heating dichloromaleintolil dichloride with piperidine and benzene in sealed tubes at 100° for 24 hours; it separates from acetone in bright yellow, transparent crystals, and melts at 107°. The crystals are monosymmetric; $a:b:c = 0·9869:0·7464$; $\beta = 63° 44'$.

γ-Paratoluididobutyrolactam, $C_6H_4Me·N\Big\langle\begin{matrix}CO\text{—}CH_2\\ \quad\ \ |\\ CH_2·CH_2\end{matrix}$, is obtained from dichloromaleinparatolil dichloride by reducing it with sodium amalgam; it crystallises from water in small needles melting at 82°, and boils at 189° under a pressure of 13 mm. Hydrolysis with barium hydroxide gives rise to *barium* γ-paratoluididobutyrate; the *silver* salt is sparingly soluble. M. O. F.

Action of Phosphorus Pentachloride on Citraconanil. By RICHARD ANSCHÜTZ and JULIUS MEYERFELD (*Annalen*, 1897, **295**, 56—66).—*Chlorocitraconanil dichloride*, $NPh\Big\langle\begin{matrix}CO\text{—}CMe\\ \quad\ \ \|\\ CCl_2·CCl\end{matrix}$, prepared from citraconanil by the action of phosphorus pentachloride, crystallises from ether in white prisms melting at 103°. Boiling water or dilute alcohol converts it into *chlorocitraconanil*, $NPh\Big\langle\begin{matrix}CO·CCl\\ \quad\ \ \|\\ CO·CMe\end{matrix}$, which crystallises from alcohol in needles melting at 135°, and boils at 190° under a pressure of 19 mm. *Chlorocitraconanilic acid*,

$COOH·CMe\!:\!CCl·CO·NHPh$, or $COOH·CCl\!:\!CMe·CO·NHPh$,

is formed on hydrolysing citraconanil with barium hydroxide, and also by the action of aniline on an ethereal solution of chlorocitraconic anhydride. *Anilidocitraconanil*, $NPh\Big\langle\begin{matrix}CO·CMe\\ \quad\ \ \|\\ CO·C·NHPh\end{matrix}$, is obtained from chlorocitraconanil and aniline, and crystallises in yellow plates melting at 157°

Chlorocitracondianil, $NPh\Big\langle\begin{matrix}CO\text{———}CMe\\ \quad\quad\quad\ \ \|\\ C(NPh)·CCl\end{matrix}$, is prepared from chlorocitraconanil dichloride and aniline, and crystallises from alcohol in slender, yellowish plates melting at 125°; further treatment with aniline at 120° yields anilidocitraconanil, and not the dianil.

Chlorocitraconimidoanil, $NPh\Big\langle\begin{matrix}CO\text{———}CMe\\ \quad\quad\quad\ \ \|\\ C(NH)·CCl\end{matrix}$, is obtained by adding

alcoholic ammonia to an ethereal solution of chlorocitraconanil dichloride, and crystallises from ether in golden yellow needles melting at 116°.

When methylic alcohol acts on chlorocitraconanil dichloride, the *compound* $C_{12}H_{12}NO_3Cl$ is produced; it separates from light petroleum in crystals belonging to the triclinic system, melts at 114°, and probably has the constitution $\mathrm{NPh}{<}\begin{array}{l}\mathrm{CO\text{———————}CMe}\\ \mathrm{C(OMe)(OH){\cdot}CCl}\end{array}$.

Chlorocitraconanil diphenyl ether, $\mathrm{NPh}{<}\begin{array}{l}\mathrm{CO\text{———}CMe}\\ \mathrm{C(OPh)_2{\cdot}CCl}\end{array}$, obtained by boiling a solution of chlorocitraconanil dichloride in benzene with phenol, separates from light petroleum in aggregates of scales melting at 125°.

a-Methyl-γ-anilidocrotonolactam (*γ-anilidotiglolactam*),

$$\mathrm{NPh}{<}\begin{array}{l}\mathrm{CO{-}CMe}\\ \mathrm{CH_2{\cdot}CH}\end{array},$$

is prepared by reducing chlorocitraconanil dichloride in ethereal solution with sodium amalgam; it crystallises in beautiful, long needles or prisms, and melts at 97—97·5°. Hydrolysis with barium hydroxide gives rise to α-methyl-γ-anilidocrotonic acid. M. O. F.

Action of Phosphorus Pentachloride on Asymmetric Dimethylsuccinanil, Dichloromaleinimide, and Succinimide. By Richard Anschütz and Georg Schroeter (*Annalen*, 1897, **295**, 67—93). —*Asymmetric dimethyldichlorosuccinanil dichloride*,

$$\mathrm{NPh}{<}\begin{array}{l}\mathrm{CO{-}CMe_2}\\ \mathrm{CCl_2{\cdot}CCl_2}\end{array},$$

is prepared by submitting *as*-dimethylsuccinanil to the action of phosphorus pentachloride at 60—70°; it crystallises from light petroleum in rhombic plates and melts at 86·5—87°, boiling at 191—192° under a pressure of 9 mm. *Asymmetric dimethyldichlorosuccinanil*,

$$\mathrm{NPh}{<}\begin{array}{l}\mathrm{CO{\cdot}CMe_2}\\ \mathrm{CO{\cdot}CCl_2}\end{array},$$

is obtained from the dichloride by the action of water, and crystallises in needles melting at 114°; it boils at 179—180·2° under a pressure of 10·5 mm. The *diphenyl ether*, $\mathrm{NPh}{<}\begin{array}{l}\mathrm{CO\text{———}CMe_2}\\ \mathrm{C(OPh)_2{\cdot}CCl_2}\end{array}$, is produced on heating a solution of the dichloride in xylene with phenol at 120—125°; it separates from benzene in lustrous crystals containing the solvent, and melts at 156—157°. The *dianil*, $\mathrm{NPh}{<}\begin{array}{l}\mathrm{CO\text{———}CMe_2}\\ \mathrm{C(NPh){\cdot}CCl_2}\end{array}$, arises from the action of aniline on the dichloride in chloroform solution; it crystallises from acetone in rosettes of prisms, and melts at 129°.

a-Dimethyl-βγ-dichloro-γ-anilidoisocrotonolactam, $\mathrm{NPh}{<}\begin{array}{l}\mathrm{CO{-}CMe_2}\\ \mathrm{CCl{:}CCl}\end{array}$, is obtained on reducing *as*-dimethyldichlorosuccinanil dichloride with sodium amalgam, and when crystallised from xylene melts at 99°; it is also produced when the dichloride is heated with mercury diphenyl and benzene at 170—180°. The dichloride is regenerated when the product is heated with phosphorus pentachloride.

Asymmetric dimethylmonochlorosuccinanil, $NPh<\begin{array}{l}CO\cdot CMe_2\\ CO\cdot CHCl\end{array}$, is produced on exposing the foregoing lactam to moist air, or by heating it with glacial acetic acid; it crystallises in small, lustrous needles, and melts at 163°.

Dichloromaleinimide chloride, $NH<\begin{array}{l}CO—CCl\\ CCl_2\cdot CCl\end{array}$, is prepared by heating dichloromaleinimide with phosphorus pentachloride in sealed tubes for 2—3 hours at 160°; it crystallises from benzene in white prisms, and melts at 147—148°; the *diphenyl ether*, $NH<\begin{array}{l}CO——CCl\\ C(OPh)_2\cdot CCl\end{array}$, is obtained by heating the dichloride with phenol and xylene at 70—80°; it crystallises from benzene in small needles, and melts at 170°.

Dichloromaleinimideanil, $NH<\begin{array}{l}CO——CCl\\ C(NPh)\cdot CCl\end{array}$, is produced by the action of aniline on an ethereal solution of dichloromaleinimide chloride, and when crystallised from glacial acetic acid melts at 151—152°.

Pentachloropyrroline, $N\leqslant\begin{array}{l}CCl\cdot CCl\\ CCl_2\cdot CCl\end{array}$, is obtained when phosphorus pentachloride acts on dichloromaleinimide (2 mols.) at 160°, and boils at 90·5° under a pressure of 10 mm.; its vapour is very irritating. Boiling water converts the substance into dichloromaleinimide, which is also produced by the action of alcohol. Reduction with sodium amalgam gives rise to tetrachloropyrroline, which Ciamician and Silber obtained on reducing perchloropyrrocoll (Abstr., 1884, 292); the tetrachloro-derivative forms lustrous leaflets, and melts and decomposes at 110°. Pentachloropyrroline is also produced when phosphorus pentachloride (4 mols.) acts on succinimide in chloroform.

The authors conclude their paper with a general discussion of the results. M. O. F.

Electro-syntheses in the Pyridine and Quinoline Groups. By Felix B. Ahrens (*Chem. Centr.*, 1896, i, 1125—1127; from *Zeit. Elektrotechn. u. Elektrochem.*, 1896, **2**, 577—581).—By the electrolysis of a solution of pyridine in 10 parts of 10 per cent. sulphuric acid, employing a lead cathode and a current density of 14 ampères per 100 sq. cm., the temperature rises to 55°, hydrogen is at length evolved, and eventually 95 per cent. of the theoretical yield of piperidine is obtained. No diaphragm is necessary, as the oxygen evolved at the anode has no action either on pyridine or piperidine. Picoline is similarly reduced to pipecoline. After frequent use, the lead cathodes become inoperative, and hydrogen is liberated without reduction. A solution of pyridine in concentrated sulphuric acid is not reduced at the cathode, but sulphur is separated and hydrogen sulphide evolved. On diluting this solution with water, and electrolysing with a low current density, using a platinum cathode, a brown, amorphous powder insoluble in acids, alkalis, water, and organic solvents, and of the composition represented by the formula $C_7H_{16}NSO_{41}$, separates, on the cathode.

The solution of a nitrosopiperidine base in 20 parts of 10 per cent. sulphuric acid is placed in the cathode vessel and this is immersed in dilute

sulphuric acid, the electrodes being of lead. A current density of 14 ampères per 100 sq. cm. at 5—6 volts. is used, and the operation carried on until hydrogen is freely evolved at the cathode, where the temperature of the liquid rises to 45—50°. Nitrosopiperidine yields pyridine and *piperylhydrazine*, $C_5NH_{10}\cdot NH_2$, a colourless, very pungent liquid boiling at 145—146°. The hydrochloride forms fine crystals, melts at 163—164°, and is easily soluble in water and alcohol; the hydrobromide is obtained in white crystals melting at 174—175°; the hydriodide crystallises in needles. The *platinochloride* crystallises in small, orange needles, sinters at 110° and froths at 116°. The hydrochloride of the benzoyl derivative, $C_5H_{11}N_2Bz,HCl$, obtained by the action of benzoic chloride on piperylhydrazine, in ethereal solution, is a white precipitate melting at 183—184° and easily soluble in water and alcohol. The free base, liberated by treatment with ammonia, crystallises in lustrous leaflets and melts at 195°.

Nitroso-α-pipecoline is similarly reduced to ammonia, α-pipecoline and *piperylmethylhydrazine*, $C_5NH_9Me\cdot NH_2$, a pungent, colourless liquid boiling at 162—165°, forming a *hydrochloride* which crystallises in white needles melting at 175°, and a *benzoyl* derivative melting at 165—166°. The *mercurochloride* forms compact crystals, which, on warming with excess of potassium hydroxide until the liquid becomes grey from separation of mercury, yields *αα-dimethyldipiperyltetrazone*, $N_2(C_5NH_9Me)_2$, which forms colourless needles or compact crystals melting at 56—57°.

Nitrosoaldehydocopellidine, on reduction by electrolysis, gives *methylethylpiperylhydrazine*, $C_5NH_8MeEt\cdot NH_2$, a very pungent liquid boiling at about 205°.

If a solution of nitrosopiperidine in 10 parts of 30 per cent. sulphuric acid and a little alcohol is placed in the porous anode vessel, this immersed in 30 per cent. sulphuric acid, and electrolysis carried on with platinum electrodes, employing a current density of 11—24 amperes per 100 sq. cm., at 4—5 volts., the temperature of the anode solution rises and the anode is attacked. *Dipiperidyl*, $C_{10}H_{20}N_2$, is produced and forms fine, colourless crystals melting at 96—97°, soluble in water, alcohol, ether, benzene, light petroleum, and chloroform, and instantly reducing silver or gold solutions. The *monobenzoyl* derivative is a colourless syrup, and its *hydrochloride* a white, crystalline precipitate. Attempts to oxidise piperidine in sulphuric acid solution, employing a current density of 14 ampères per 100 sq. cm. at 3·7—4·6 volts., failed.

By electrolysing a solution of quinoline in 20 parts of 10 per cent. sulphuric acid in the same way as nitrosopiperidine, but employing a current density of 17 ampères per 100 sq. cm. at 5·5 volts., tetrahydroquinoline, C_9NH_{11}, dihydroquinoline, $(C_9NH_9)_2$, and the polymeric dihydroquinoline, $(C_9NH_9)_3$, which sinters at 58° and melts below 80° to a clear, viscous liquid, are formed. By the action of hydrochloric acid and sodium nitrite, this compound forms the nitroso-derivative, $(C_9NH_8\cdot NO)_3$, as a greenish-yellow precipitate, which, on warming with tin and hydrochloric acid, is partially reduced to tetrahydroquinoline. A red liquid is formed at the anode which yields lustrous, brown needles and is capable of dyeing wool yellowish-green directly in sulphuric acid solution.

On electrolysis in the same way as quinoline, quinaldine yields *tetrahydroquinaldine*, $C_{10}H_{13}N$, and *dihydroquinaldine*, $(C_{10}H_{11}N)_3$, a white, amorphous powder which, on melting, behaves like the corresponding dihydroquinoline, and resembles it also in its solubility in the various reagents. It forms a yellow nitroso-compound, $(C_{10}H_{10}N \cdot NO)_3$.

E. W. W.

Mercuropiperidine Compounds. By F. CERDELLI (*Gazzetta*, 1897, **27**, i, 18—23).—On saturating a hot, aqueous solution of piperidine sulphate with yellow mercuric oxide, filtering, and allowing to cool, *mercuropiperidine sulphate*, $Hg(C_5H_{11}N)_2SO_4$, separates in lustrous, colourless prisms containing $6H_2O$, of which $5H_2O$ is lost over sulphuric acid; it decomposes at 100°, and when its aqueous solution is treated with barium carbonate, carbonic anhydride and piperidine are liberated, and *mercuropiperidine hydroxide*, $Hg(C_5H_{11}N \cdot OH)_2$, remains in solution. The hydroxide reacts with potassium iodide in accordance with the following equation, $Hg(C_5H_{11}N \cdot OH)_2 + 2KI = 2C_5H_{11}N + HgI_2 + 2KHO$.

A double *compound* of the composition $3Hg(C_5H_{11}NCl)_2,HgCl_2$, separates in colourless needles on cooling a solution of mercuric chloride in piperidine; it is decomposed by water, and on treatment with hydrogen sulphide yields piperidine hydrochloride and mercuric sulphide. A *compound* of the composition $2Hg(C_5H_{11}NCl)_2,HgCl_2$ separates as a white, amorphous powder on mixing aqueous solutions of mercuropiperidine sulphate and sodium chloride. W. J. P.

Organo-mercuric Compounds derived from α-Picoline. By G. GARBARINI (*Gazzetta*, 1897, **27**, i, 23—27).—The author has prepared salts of mercuro-α-picoline analogous to those of mercuropyridine obtained by Pesci (Abstr., 1896, i, 388).

Mercuro-α-picoline sulphate, $Hg(C_6H_7N)_2SO_4$, separates in colourless needles containing $3 \cdot 5H_2O$, on cooling a solution of mercuric sulphate in aqueous α-picoline solution; it loses its water over sulphuric acid, and decomposes at about 200° without melting. The *hydroxide*, obtained in solution by decomposing the sulphate with barium carbonate, reacts with potassium iodide similarly to mercuropiperidine hydroxide (compare preceding abstract). Mercuric chloride dissolves in α-picoline with development of heat, and on cooling the saturated solution, lustrous, colourless needles of a double *compound* of the composition $5Hg(C_6H_7NCl)_2,HgCl_2$, which melts at 170—172°, are deposited. Microscopic, colourless needles of a double *compound* of the composition $Hg(C_6H_7NCl)_2,HgCl_2$ separate on mixing alcoholic solutions of α-picoline and mercuric chloride. W. J. P.

Addition of Methylic Iodide to Methylquinaldone. By LUDWIG KNORR (*Ber.*, 1897, **30**, 922—926).—When methylquinaldone is heated at 100° with methylic iodide, the pseudomethiodide is formed, identical with the methiodide of γ-methoxyquinaldine (Conrad and Eckhardt, Abstr., 1889, 519). Methylquinaldone, therefore, behaves towards methylic iodide in an analogous manner to antipyrine, which it also resembles in constitution. A. H.

An Additive Compound of Methylquinaldone and Benzoic Chloride. By LUDWIG KNORR and PAUL RABE (*Ber.*, 1897, **30**,

927—928. Compare the foregoing abstract).—Methylquinaldone also resembles antipyrine in its behaviour towards benzoic chloride, forming an unstable *additive compound*, which crystallises in small, faintly-red needles. When rapidly heated, it melts at 112°, then again solidifies, and when further heated melts at 158—160°. If slowly heated, it softens at 115—120° and melts at 160—161°. In its reactions, it closely resembles antipyrine chlorobenzoylate (this vol., i, 110), and it is probable that the two substances have a similar constitution. Aqueous soda converts it into methylquinaldone, sodium chloride and benzoate being formed. A. H.

Behaviour of the Oxygen Ethers of Carbostyril and 2′-Hydroxy-4′-lepidine towards Alkyl Halogen Derivatives. By LUDWIG KNORR (*Ber.*, 1897, **30**, 929—933. Compare the two foregoing abstracts).—The nitrogen ethers of the α-quinolones, such as methyllepidone, $C_6H_4<\begin{matrix}CMe:CH\\ NMe\cdot CO\end{matrix}$, do not yield methiodides when heated with methylic iodide, and thus differ from the corresponding derivatives of γ-quinaldine and 1′-phenyl-3′-methylpyrazolone.

The oxygen ethers of the α-quinolones, on the other hand, are converted by methylic iodide into the nitrogen methyl ethers, the change taking place completely and rapidly on warming, slowly in the cold. Thus, when 2′-ethoxyquinoline, $C_6H_4<\begin{matrix}CH:CH\\ N=C\cdot OEt\end{matrix}$, is heated with methylic iodide, it is converted into methylquinolone,

$$C_6H_4<\begin{matrix}CH:CH\\ NMe\cdot CO\end{matrix},$$

Ethoxylepidine, $C_6H_4<\begin{matrix}CMe:CH\\ N=C\cdot OEt\end{matrix}$, and methoxylepidine, when treated in a similar manner, yield methyllepidone.

It seems probable that quaternary iodides are formed as intermediate products in these reactions, but none of these has yet been isolated. The reaction is otherwise strictly analogous to that which occurs with antipyrine, the pseudomethiodide of which is unstable, and with the alkyl-4′-quinolones, the pseudomethiodides of which are stable, and can readily be prepared. A. H.

Behaviour of 4′-Methoxy-2′-phenylquinoline towards Methylic Iodide. By LUDWIG KNORR and EDUARD FERTIG (*Ber.*, 1897, **30**, 937—940. Compare preceding abstract).—4′-Methoxy-2′-phenylquinoline resembles 2′-methoxylepidine in being directly converted by methylic iodide into the isomeric 2′-phenyl-1′-methyl-4′-quinolone, without the formation of a stable intermediate product. This difference between the behaviour of this substance and of 4′-methoxyquinoline is probably due to the acidifying effect of the phenyl group.

4′-Chloro-2′-phenylquinoline, obtained by the action of phosphorus pentachloride on 2′-phenyl-4′-quinolone, melts at 63—64°; when treated with a solution of sodium methoxide, it yields *4′-methoxy-2′-phenylquinoline*, $C_6H_4<\begin{matrix}C(OMe):CH\\ N\text{———}CPh\end{matrix}$, which crystallises in needles

melting at 69—70°, and is slowly volatile with steam. When this substance is heated with methylic iodide, it passes into the isomeric *2′-phenyl-1′-methyl-4′-quinolone*, $C_6H_4<\begin{matrix}CO—CH\\NMe\cdot CPh\end{matrix}$, which crystallises in lustrous plates melting at 85°, and is not volatile with steam.

A. H.

1-Quinolyloxyacetic Acid. By OSKAR NAGEL (*Monatsh.*, 1897, **18**, 31—43).—When an alcoholic solution of 1-hydroxyquinoline (1 mol.) is added to alcoholic sodium ethoxide (2 mols.), the product dissolved by the gradual addition of water, an alcoholic solution of chloracetic acid added, and the whole heated on the water bath for 12 hours, 50 per cent. of the hydroxyquinoline can be recovered unchanged, but *1-quinolyloxyacetic acid*, $C_9NH_6\cdot O\cdot CH_2\cdot COOH$, can be isolated from the product of the action. This acid melts at 176° (uncorr.), loses carbonic anhydride when further heated, and yields a *dibromo*-derivative which melts at 203°. Its *silver*, $C_{11}H_8NO_3Ag$, *barium* $(C_{11}H_8NO_3)_2Ba + 3H_2O$, and *potassium*, $C_{11}H_8NO_3K + H_2O$, salts were prepared; also the *hydrochloride*, $C_{11}H_9NO_3,HCl$, melting at 216°; the orange-yellow *platinochloride* $(C_{11}H_9NO_3)_2,H_2PtCl_6 + 2H_2O$, melting and decomposing at 210°; the *stannochloride*, $C_{11}H_9NO_3,HSnCl_3 + H_2O$; a compound with mercuric chloride, $(C_{11}H_9NO_3)_2,HgCl_2 + 3H_2O$; the *hydriodide*, $C_{11}H_9NO_3,HI + 2H_2O$, melting at 193°; and the *sulphate*,

$$C_{11}H_9NO_3,H_2SO_4 + 2H_2O,$$

melting at 115°. The acid character is more pronounced than the basic.

C. F. B.

Synthesis of Isoquinoline and its Derivatives. By CÆSAR POMERANZ (*Monatsh.*, 1897, **18**, 1—5. Compare Abstr., 1894, i, 552).—The derivatives described were obtained by condensing a derivative of benzaldehyde or benzophenone with amidoacetal, dissolving the product in strong sulphuric acid, the mixture being kept cool with ice, allowing it to remain for 2 hours, and then adding half the volume of phosphorus oxychloride and heating for $\frac{1}{4}$-hour over a naked flame. Of the first compound described, the yield was 20 per cent. of the theoretical; of the last two, enough was not obtained for a combustion.

1-Methylisoquinoline, from orthomethylbenzaldehyde, boils at 258°; the red *platinochloride*, $(C_9NH_6Me)_2,H_2PtCl_6 + 2H_2O$, and yellow *picrate*, melting at 204—205°, were prepared. *3-Methylisoquinoline*, from paramethylbenzaldehyde, melts at 83° and boils at 263—264° (uncorr.); the *platinochloride* and *picrate*, the latter melting at 212°, resemble those of the 1-methyl compound in appearance and composition. *1-Chlorisoquinoline*, from orthochlorobenzaldehyde, melts at 55°, and yields a red *platinochloride*, $(C_9NH_6Cl)_2,H_2PtCl_6$. *1′-Phenylisoquinoline*, from benzophenone, melts at 87—88°; the *platinochloride*,

$$(C_9NH_6Ph)_2,H_2PtCl_6,$$

is red.

C. F. B.

Synthesis of 3′-Isopropylisoquinoline and of 3′-Butylisoquinoline. By J. N. LEHMKUHL (*Ber.*, 1897, **30**, 889—897).—Using Gabriel and Neumann's method for the preparation of alkylated

derivatives of isoquinoline, the following compounds have been isolated.

ψ-Di-isobutyrylorthocyanobenzylic cyanide,

$$CN\cdot C_6H_4\cdot C(CN){:}CPr^\beta\cdot O\cdot COPr^\beta,$$

is prepared by condensing orthocyanobenzylic cyanide and isobutyric anhydride; when crystallised from alcohol, it contains 1 mol. EtOH and melts at 140°; on hydrolysing this compound with aqueous potassium hydroxide, 3′ : 4′-*isopropylcyanoisocarbostyril*, $C_6H_4{<}\begin{matrix}C(CN){:}CPr^\beta \\ CO\text{——}NH\end{matrix}$, is produced, a compound crystallising from alcohol in pale yellow needles, and melting with partial decomposition at 227—229°; as a bye-product in this reaction, there is also formed *α-orthodicyano-β-ethoxyamenylbenzene*, $CN\cdot C_6H_4\cdot C(CN){:}CPr^\beta\cdot OEt$, a substance crystallising from alcohol in well formed needles melting at 91°.

By the action of methylic iodide on 3′ : 4′-isopropylcyanoisocarbostyril, 2′ : 3′ : 4′-*methylisopropylcyanoisocarbostyril*, $C_6H_4{<}\begin{matrix}C(CN){:}CPr^\beta \\ CO\text{——}NMe\end{matrix}$, is produced, which crystallises from alcohol in colourless needles melting at 200°—210°; both from the methyl derivative as well as from the unmethylated compound, the cyano-group can be eliminated by hydrolysis with concentrated sulphuric acid, yielding 3′-*isopropylisocarbostyril*, $C_6H_4{<}\begin{matrix}CH{:}CPr^\beta \\ CO\cdot NH\end{matrix}$, which crystallises from alcohol in colourless crystals melting at 186—189°, and the corresponding 2′-*methyl* derivative, which forms colourless needles melting at 184—186°. On treating 3′-isopropylisocarbostyril with phosphorus oxychloride, 1′ : 3′-chlorisopropylisoquinoline, $C_6H_4{<}\begin{matrix}CH{:}C\cdot Pr^\beta \\ CCl\cdot N\end{matrix}$, is formed; this is a colourless liquid boiling at 292—293° (748 mm.), and on reduction with phosphorus and hydriodic acid yields 3′-*isopropylisoquinoline*, $C_6H_4{<}\begin{matrix}CH{:}CPr^\beta \\ CH{:}N\end{matrix}$, a colourless liquid boiling at 264—266° (771 mm.), and forming a *platinochloride* consisting of yellow needles melting at 180—182°, an *aurochloride* crystallising in needles, and a yellow *picrate*.

On treatment with sodium and methylic alcohol, chlorisopropylisoquinoline yields 1′ : 3′-*methoxyisopropylisoquinoline*, $C_6H_4{<}\begin{matrix}CH\text{===}CPr^\beta \\ C(OMe){:}N\end{matrix}$, a colourless oil boiling at 268—270° (772 mm.), and having slightly basic properties; the corresponding *ethoxy*-derivative boils at 283—285° (771 mm.), the *phenoxy*-compound is a dark brown oil which does not distil unchanged; all these compounds yield yellow, crystalline *platinochlorides*.

On condensing orthocyanobenzylic cyanide with valeric anhydride, *ψ-divalerylorthocyanobenzylic cyanide*,

$$CN\cdot C_6H_4\cdot C(CN){:}C(C_4H_9)\cdot O\cdot CO\cdot C_4H_9,$$

is formed; this crystallises from alcohol in colourless plates melting at 153—154°. 3′ : 4′-*Butylcyanoisocarbostyril*, $C_6H_4{<}\begin{matrix}C(CN){:}C\cdot C_4H_9 \\ CO\text{——}NH\end{matrix}$, crys-

tallises from alcohol in pale yellow needles melting at 227—229°, a similar bye-product as in the former case, namely, *ortho-α-dicyano-β-ethoxyhexenylbenzene*, $CN\cdot C_6H_4\cdot C(CN){:}C(C_4H_9)\cdot OEt$, being also formed; after recrystallisation from alcohol, this melts at 72°.

3′-Butylisocarbostyril, $C_6H_4<\begin{matrix}CH\cdot C\cdot C_4H_9\\ CO\cdot NH\end{matrix}$, crystallises in brown plates melting at 138—139°; the liquid *1′:3′-chlorobutylisoquinoline*, $C_6H_4<\begin{matrix}CH{:}C\cdot C_4H_9\\ CCl{:}N\end{matrix}$, boils at 298—300° (758 mm.), and gives a yellow, crystalline *platinochloride*; on reduction, the chloro-compound yields *3′-butylisoquinoline*, $C_6H_4<\begin{matrix}CH{:}C\cdot C_4H_9\\ CH{:}N\end{matrix}$, a slightly coloured oil boiling at 278° (745 mm.), which has only feebly basic properties, but yields, however, a well-defined crystalline *platinochloride*. J. F. T.

Constitution of Acid Derivatives of 1-Phenyl-3-methyl-5-pyrazolone. By Friedrich Stolz (*J. pr. Chem.*, 1897 [ii], **55**, 145—171).—The compounds obtained by Nef, Himmelbauer, and others, by the action of benzoic chloride, acetic chloride, benzylic chloride, ethylic chloroformate, and ethylic acetate on 1:3-phenyl-methyl-5-pyrazolone in the presence of aqueous sodium hydroxide, and thought by them to be 2-derivatives of the pyrazolone with formulæ such as $NPh<\begin{matrix}NBz\cdot CMe\\ CO—CH\end{matrix}$, are shown to be in reality 5-derivatives of the isomeric pyrazole, having the formulæ $NPh<\begin{matrix}N=\!=\!=CMe\\ C(OBz){:}CH\end{matrix}$, &c. In the first place, the benzoyl derivative yields, by direct addition in benzene solution, a *methiodide* melting and decomposing at 188°, and this is readily converted, by warming with dilute sodium hydroxide, into antipyrine, benzoic acid, and hydriodic acid; it would be difficult to reconcile this ready formation of antipyrine with the first of the two formulæ given above. Secondly, they do not exhibit the characteristic reactions of antipyrine (colorations with ferric chloride and with nitrous acid, sparing solubility in ether and light petroleum), but have rather the character of alkoxy-compounds. It may be added that 4-derivatives of pyrazolone are often simultaneously formed in the reaction. There seems, however, to be no way of getting 2-derivatives by the direct action of the acid chlorides, &c., on phenylmethyl-pyrazolone. Nor can these be synthesised by the action of acetyl-, formyl-, or benzoyl-phenylhydrazine on ethylic acetoacetate; such action in the presence of phosphorus trichloride results in the formation of the diacidylhydrazine, together with 1:3-phenyl-methyl-5-pyrazolone, and usually some 1:5-phenylmethyl-3-pyrazolone and other products. They can, however, be obtained by acting on a 5-alkoxypyrazole derivative and then hydrolysing the alkoxy-group with alkali.

Himmelbauer's 1:2:3-*phenylbenzylmethyl* 5-*pyrazolone*, melting at 134—136°, is in reality the 1:4:3:5 compound, and had already been discovered twice. The 1:2:3:5 compound, $C_{17}H_{16}N_2O,H_2O$, can, however, be obtained by heating phenylmethylpyrazolone with

benzylic chloride for 12 hours at 120°; when anhydrous, it melts at 119°.

1-*Parethoxyphenyl*-3-*methyl*-5-*acetoxypyrazole* is obtained by treating ethoxyphenylmethylpyrazolone in alkaline solution with acetic anhydride; it melts at 76°. 4-*Acetyl*-1 : 3-*phenylmethyl*-5-*pyrazolone* is obtained by boiling commercial "pyrazolone" with acetic anhydride and sodium acetate; it melts at 58°; the acetyl group is removed by boiling with hydrochloric acid, "pyrazolone" being re-formed; it is remarkable that sodium hydroxide does not effect this change.

1 : 3-*Phenylmethyl*-5-*pyrazolone*-2-*acetic acid* was obtained by heating phenylmethyl-5-ethoxypyrazole with ethylic iodacetate for 12 hours at 100° and warming the product with aqueous sodium hydroxide; it melts and decomposes at 205—207°; the *ethylic salt* melts at 118°.

1 : 3-*Phenylmethylpyrazole*-5-*oxyacetic acid* is obtained by adding sodium ethoxide and then ethylic chloracetate to an alcoholic solution of phenylmethylpyrazolone and hydrolysing the ethylic salt thus formed; it melts at 158°; the *methylic* and *ethylic* salts melt at 78° and 47° respectively.

1 : 3 : 4-*Phenyldimethyl*-5-*pyrazolone*-2-*acetic acid* (Himmelbauer's 4-acetic acid), obtained by the action of ethylic bromacetate on phenyldimethyl-5-ethoxypyrazole and subsequent hydrolysis of the product, melts and decomposes at 215° (Himmelbauer 190°); the *methylic* salt melts at 112°. 1 : 3 : 4-*Phenyldimethyl*-5-*pyrazolone*-4-*acetic acid* (Himmelbauer's 2-acetic acid) is formed, together with the preceding acid, when an alkaline solution of phenyldimethylpyrazolone is boiled for half an hour with chloracetic acid; it melts at 103°; the *methylic* salt melts at 143°, and differs from that of the preceding acid in being insoluble in water, from that of the following acid by its lesser solubility in methylic alcohol. 1 : 3 : 4-*Phenyldimethylpyrazole*-5-*oxyacetic acid* is obtained by boiling an alcoholic solution of phenyldimethylpyrazolone and sodium ethoxide with ethylic chloracetate and hydrolysing the product; it melts at 141°, its *methylic* salt at 55°.

Among the products of the action of formyl- and of benzoyl-phenylhydrazine on ethylic acetoacetate, there was obtained in both cases an orange-yellow substance melting at 180°. This can also be obtained from "pyrazolone" and formic acid, and it is identical with the products obtained respectively by Knorr from 1 : 3-phenylmethyl-5-pyrazolone with chloroform and alkali, and by Pellizzari from phenylmethylpyrazolone and paraformaldehyde, and also by the loss of water from 1 : 3-phenylmethyl-4-methoxy-5-pyrazolone. Molecular weight-determinations lead to the formula $NPh<\begin{array}{l}N{=}CMe \qquad CMe{:}N\\ CO\cdot CH\cdot CH{:}C{-}CO\end{array}>NPh$ for this substance. C. F. B.

Compounds of Antipyrine with the Cresols. By GUSTAVE PATEIN and E. DUFAU (*Bull. Soc. Chim.*, 1896, [iii], **15**, 609—610).—*Orthocresol-antipyrine*, $C_6H_4Me\cdot OH,C_{11}H_{12}N_2O$, is formed when orthocresol is fused with antipyrine. From alcohol, it crystallises in colourless crystals melting at 60—62°, which are very slightly soluble in water and ether, but more soluble in chloroform. On mixing an alcoholic solution

of metacresol with an aqueous solution of antipyrine, an oily liquid separates, which, on standing for some time, deposits crystals of antipyrine, the residual liquid then having the composition corresponding with the union of the two substances in molecular proportion. It is almost odourless, soluble in alcohol and ether, and partially decomposed by water. When allowed to remain over sulphuric acid, it undergoes slow decomposition, antipyrine crystallising out, and the cresol being disengaged in the state of vapour, the composition of the liquid therefore remaining constant. When paracresol is substituted for the meta-compound in the above experiment, analogous results are obtained, an oily compound of 1 mol. of the cresol with 1 mol. of antipyrine being obtained. A. C. C.

Formation of Pyrimidones. By SIEGFRIED RUHEMANN (*Ber.*, 1897, **30**, 821—823).—Ethylic dicarboxyglutaconate reacts with amidines to produce derivatives of pyrimidone, according to the equation $NH_2\cdot CR\colon NH + (COOEt)_2CH\colon C(COOEt)_2 = CH_2(COOEt)_2 + C_2H_6O + R\cdot C{<}{}^{N\text{——}CO}_{NH\text{—}CH}{>}C\cdot COOEt$.

Ethylic phenylpyrimidonecarboxylate, $CPh{<}{}^{N\text{——}CO}_{NH\cdot CH}{>}C\cdot COOEt$, is obtained by heating an alcoholic solution of benzamidine hydrochloride, sodium ethoxide, and ethylic dicarboxyglutaconate. It crystallises in colourless needles melting at 214°, and is only very sparingly soluble in alkalis. The free *acid* crystallises in small prisms, melts at 265°, and is sparingly soluble in boiling water. The *silver* salt has the composition $C_{11}H_6Ag_2N_2O_3$. Ethylic phenylpyrimidonecarboxylate dissolves in warm, aqueous ammonia, yielding a solution from which silver nitrate precipitates a gelatinous *silver* salt, $C_{13}H_{11}AgN_2O_3$. When this is heated with ethylic iodide, it is converted into an ethyl ether, which appears to be a mixture of the two possible isomeric ethers, $CPh{<}{}^{N\text{——}CO}_{NEt\cdot CH}{>}C\cdot COOEt$ and $CPh{<}{}^{N\cdot C(OEt)}_{N\text{===}CH}{>}C\cdot COOEt$.

A. H.

Action of Ethylic Oxalate on Aromatic Amines. II. By RICHARD E. MEYER (*Ber.*, 1897, **30**, 768—770. Compare this vol., i, 45).—The dioxyquinoxaline prepared by the author from ethylic oxalate, and orthotolylenediamine [1 : 3 : 4] is now found to be identical with the compound obtained by Hinsberg from oxalic acid on condensation with the same base. Hinsberg assigns the formula

$$C_6H_4{<}{}^{N\colon C\cdot OH}_{N\colon C\cdot OH}$$

to this substance, whilst its preparation from ethylic oxalate, and the fact that ethylic alcohol is eliminated during the process of condensation, would seem to indicate the formula $C_6H_4{<}{}^{NH\cdot CO}_{NH\cdot CO}$. The general reactions of the substance can be explained by the use of either formula. J. F. T.

Diamidophenylosotriazole. By JOHANNES THIELE and KARL SCHLEUSSNER (*Annalen*, 1897, **295**, 129—172).—*Oxalenphenylhydrazidamidoxime*, $NHPh\cdot N\!:\!C(NH_2)\cdot C(NH_2)\!:\!NOH$, obtained by heating a concentrated alcoholic solution of dicyanophenylhydrazine with an aqueous solution of hydroxylamine (1 mol.), crystallises from ethylic acetate in lustrous scales melting at 174°; the solution in alkalis rapidly becomes dark red, and a red coloration is also developed with ferric chloride. The *acetyl* derivative, which is likewise readily oxidised, crystallises from alcohol in scales and melts at 146°.

Diamidophenylosotriazole, $NPh<\begin{matrix}N\!:\!C\cdot NH_2\\ | \\ N\!:\!C\cdot NH_2\end{matrix}$, is produced when the foregoing oxime is heated with 6 parts of water at 150° during 2 hours, and crystallises from water in long, colourless needles melting at 143°; the aqueous solution is neutral, and exhibits strong reducing action, a deep indigo-blue coloration being developed by ferric chloride and bromine water, whilst a solution in hydrochloric acid stains fir-wood deep red. When alkaline solutions are heated at 150—200°, a reddish-brown, infusible condensation product is formed, insoluble in ordinary solvents; fuming hydrochloric acid at 200° completely decomposes the base, and the production of phenylprozane, $NH_2\cdot NPh\cdot NH_2$, could not be established. The *hydrochloride* of diamidophenylosotriazole crystallises from water or dilute alcohol in leaflets, and melts at 210°, whilst the *sulphate* crystallises in plates; the *picrate* crystallises in fascicular aggregates of needles and melts at 153°. The *silver nitrate* compound crystallises in colourless leaflets and melts and totally decomposes at 150°; the solutions rapidly become blue.

Diamidophenylosotriazolesulphonic acid, $SO_3H\cdot C_6H_4\cdot N<\begin{matrix}N\!:\!C\cdot NH_2\\ | \\ N\!:\!C\cdot NH_2\end{matrix}$, obtained by dissolving the base in 8 or 10 per cent. fuming sulphuric acid, forms colourless needles very sparingly soluble in water; the solution, however, develops an intense brown coloration with bromine, the liquid, whilst indifferent towards mineral acids, being decolorised by alkalis. The *sodium* salt crystallises in colourless plates, and the *ammonium* salt separates from water in colourless needles.

The *azine* of diamidophenylosotriazole,

$$NPh<\begin{matrix}N\!:\!C\cdot N\\ | \\ N\!:\!C\cdot N\end{matrix}>C_6H_3\cdot N<\begin{matrix}N\!:\!C\cdot NH_2\\ | \\ N\!:\!C\cdot NH_2\end{matrix},$$

is a blue, amorphous substance, obtained by oxidising the triazole in 1 per cent. hydrochloric acid with ferric chloride; stannous chloride and hydrochloric acid reduce it to the *leuco*-compound, which crystallises in colourless needles and melts, when anhydrous, at 175°. The *quinoxaline* from diamidophenylosotriazole and benzile,

$$NPh<\begin{matrix}N\!:\!C\cdot N\!:\!CPh\\ | \quad\quad | \\ N\!:\!C\cdot N\!:\!CPh\end{matrix},$$

crystallises from glacial acetic acid in deep red needles, and melts at 217°; concentrated sulphuric acid dissolves it with a deep violet coloration, which becomes red on dilution with water. The *quinoxaline* from diamidophenylosotriazole and phenanthraquinone,

$$NPh<\begin{matrix}N\!:\!C\cdot N\!:\!C\cdot C_6H_4\\ | \quad\quad | \quad | \\ N\!:\!C\cdot N\!:\!C\cdot C_6H_4\end{matrix},$$

crystallises from chloroform in needles, and melts at 289°; the solution in concentrated sulphuric acid is deep indigo blue. *Dibenzylidenediamidophenylosotriazole*, $\mathrm{NPh}<\begin{matrix}\mathrm{N{:}C\cdot N{:}CHPh}\\ \mathrm{N{:}\dot{C}\cdot N{:}CHPh}\end{matrix}$, separates from glacial acetic acid in yellowish, prismatic crystals, and melts at 162°; *dihydroxybenzylidenediamidophenylosotriazole* crystallises in yellow needles and melts at 210°.

The *monacetyl* derivative of diamidophenylosotriazole dissolves more readily in water than the acetyl derivative, and crystallises in needles melting at 186°; when prepared in the ordinary manner, it is associated with the diacetyl derivative, and is therefore more conveniently obtained by heating that compound with diamidophenylosotriazole at 200—210° during 4 hours. The *diacetyl* derivative forms colourless, prismatic crystals and melts at 206°. The *dibenzoyl* derivative melts at 242°.

Amidodiazophenylosotriazole, $\mathrm{NPh}<\begin{matrix}\mathrm{N{:}C\cdot N{:}N\cdot OH}\\ \mathrm{N{:}\dot{C}\cdot NH_2}\end{matrix}$, is obtained by adding a solution of diamidophenylosotriazole hydrochloride to a cold solution of free nitrous acid, an amorphous, greenish-yellow, insoluble compound being produced when this order of procedure is reversed; the *picrate* crystallises in needles, and melts and decomposes at 121°.

Dimethylanilineazoamidophenylosotriazole,

$$\mathrm{NPh}<\begin{matrix}\mathrm{N{:}C\cdot N{:}N\cdot C_6H_4\cdot NMe_2}\\ \mathrm{N{:}\dot{C}\cdot NH_2}\end{matrix},$$

crystallises from alcohol in red needles and melts and decomposes at 243°; it dyes wool orange yellow, and forms an intense cochineal red solution with concentrated sulphuric acid.

Phenylosotriazoleazimide, $\mathrm{NPh}<\begin{matrix}\mathrm{N{:}C\cdot NH}\\ \mathrm{N{:}\dot{C}-\!-N}\end{matrix}>\mathrm{N}$, is formed when a solution of amidodiazophenylosotriazole is heated on the water bath with sodium acetate; it crystallises from water in colourless needles, becomes brown at 130—140° and when exposed to air is insoluble in petroleum, and melts at 147°. The substance is indifferent towards potassium permanganate and an ammoniacal solution of silver nitrate, and undergoes no change when treated with cold dilute mineral acids; hot 50 per cent. sulphuric acid, however, effects a rupture of the azimide ring, a result which is also brought about under the influence of acetic chloride, the acetyl derivative of amidodiazophenylosotriazole being produced. The *acetyl* derivative of the azimide, $\mathrm{NPh}<\begin{matrix}\mathrm{N{:}C\cdot NAc}\\ \mathrm{N{:}\dot{C}-\!-N}\end{matrix}>\mathrm{N}$, is prepared by diazotising the monacetyl derivative of diamidophenylosotriazole, and treating the liquid with a concentrated solution of sodium acetate; it is colourless, and explodes at 160°. Whilst phenylosotriazoleazimide is relatively stable towards mineral acids, boiling acetic acid decomposes the acetyl derivative, forming the *acetyl* derivative of amidodiazophenylosotriazole chloride, $\mathrm{NPh}<\begin{matrix}\mathrm{N{:}C\cdot NHAc}\\ \mathrm{N{:}\dot{C}\cdot N{:}N\cdot Cl}\end{matrix}$, which melts and decomposes at 150—155°, and rapidly becomes yellow and loses hydrogen chloride when exposed to air; mineral acids convert it into the acetyl

derivative of phenylosotriazoleazimide, and hot caustic soda gives rise to phenylosotriazoleazimide. The *acetyl* derivative of amidophenylosotriazole, $NPh<\begin{matrix}N:C\cdot NHAc\\ |\\ N:CH\end{matrix}$, is obtained by treating the acetyl derivative of phenylosotriazoleazimide with boiling alcohol, aldehyde and nitrogen being eliminated; it crystallises in colourless needles and melts at 166°.

Amidophenylosotriazole, $NPh<\begin{matrix}N:C\cdot NH_2\\ |\\ N:CH\end{matrix}$, is prepared from the acetyl derivative, and crystallises from hot water in long, colourless needles, melting at 70°; it behaves as a feeble reducing agent towards ammoniacal silver nitrate, and is coloured pale blue by ferric chloride, probably owing to contamination with diamidophenylosotriazole.

Amidohydroxyphenylosotriazole, $NPh<\begin{matrix}N:C\cdot OH\\ |\\ N:C\cdot NH_2\end{matrix}$, is a bye-product in the preparation of oxalenphenylhydrazidamidoxime, occurring in the residual alkaline liquid after removing diamidophenylosotriazole; it crystallises from water in long, colourless needles, and melts and decomposes at 181°. The aqueous solution is acidic, and stains a fir splint of an intense reddish-yellow; ferric chloride produces a beautiful, violet colouring matter. The *benzylidene* derivative crystallises from dilute alcohol and melts at 173°. *Diazohydroxyphenylosotriazole*, $NPh<\begin{matrix}N:C\cdot N:N\cdot OH\\ |\\ N:C\cdot OH\end{matrix}$, is prepared by adding a dilute alcoholic solution of hydroxyamidophenylosotriazole to a well-cooled solution of nitrous acid; it is a very unstable substance, and in a few days loses the property of combining with sodium β-naphtholdisulphonate. When the solution in sulphuric acid is treated with finely-divided metallic copper, nitrogen is eliminated, and *hydroxyphenylosotriazole*, $NPh<\begin{matrix}N:C\cdot OH\\ |\\ N:CH\end{matrix}$, is produced; it crystallises from hot water in long, colourless needles, and melts at 124°.

β-Naphthylamidazohydroxyphenylosotriazole,

$$NPh<\begin{matrix}N:C\cdot N:N\cdot C_{10}H_6\cdot NH_2\\ |\\ N:C\cdot OH\end{matrix},$$

is obtained from diazohydroxyphenylosotriazole and β-naphthylamine; it is brownish-red, and dissolves in concentrated sulphuric acid with an indigo-blue coloration.

Cyanosemicarbazide, $C_2(NH_2)_2(N\cdot NH\cdot CO\cdot NH_2)_2$, produced when cyanogen in alcoholic solution acts on amidoguanidine, crystallises from water in colourless needles which melt and decompose at 223°; the aqueous solution is acidic, and reduces ammoniacal silver nitrate solution.

Dicyanosemicarbazide, $NH_2\cdot C(CN):N\cdot NH\cdot CO\cdot NH_2$, obtained from cyanogen and semicarbazide, crystallises in fascicular aggregates of colourless needles, and when heated does not melt, but slowly chars, yielding ammonia and hydrogen cyanide; alkalis dissolve and partly decompose it. The *amidoxime*, $NH_2\cdot C(NOH)\cdot C(NH_2):N\cdot NH\cdot CO\cdot NH_2$,

obtained by the action of hydroxylamine, crystallises from water in colourless needles; it closely resembles dicyanosemicarbazide, but ferric chloride develops a pale yellow coloration, whilst the oxime becomes dark reddish-brown. The *compound*, $C_3H_5N_5O_2$, is produced when a solution of the oxime in water is heated at 160° during 2 hours and subsequently acidified with acetic acid; it separates from hot water in colourless crystals, and is insoluble in the usual organic solvents. The *compound*, $C_6H_{14}N_8O_7$, which remains in the liquid after the foregoing substance has been precipitated with acetic acid, crystallises in silky, infusible needles; the solution in dilute acetic acid becomes pale red with bromine, the colour being destroyed by mineral acids or by excess of the halogen. It decolorises potassium permanganate immediately, and reduces an ammoniacal solution of silver; mineral acids and alkali carbonates at 140—150° eliminate carbonic anhydride and hydrazine.

Phenylhydrazidoxalhydroxamic acid, NHPh·NH·CO·CO·NH·OH or NHPh·NH·CO·C(OH):NOH, obtained by the action of hydroxylamine (2 mols.) on ethylic phenylhydrazinoxalate, crystallises from methylic alcohol in colourless scales which melt and decompose at 172°; it is very sparingly soluble in common media, but dissolves in alkalis, and after precipitation with acetic acid melts at 178—180°. Ferric chloride develops a violet-red coloration, and boiling glacial acetic acid completely decomposes the substance, yielding a small quantity of phenylurazole; hot soda converts it into phenylhydrazidooxalic acid. The *acetyl* derivative, NHPh·NH·CO·C(OH):NOAc, separates from acetic acid in pale yellow crystals, and melts at 147°; when heated with 6 to 8 parts of dimethylamine at about 150°, phenylurazole is formed.

Phenylurazole melts at 262° (Pinner, Abstr., 1887, 1042); the *monosodium* and *sodium* derivatives are crystalline, the diacetyl derivative melts at 162—163° (compare *loc. cit.*), and the *monacetyl* derivative crystallises from water or benzene in colourless needles, and melts at 170°. M. O. F.

3 : 6-Dihydroxyxanthone. By RICHARD MEYER and ALFRED CONZETTI (*Ber.*, 1897, **30**, 969—973).—On fusing fluorescein chloride with potash at 270—280° and acidifying the product, a large quantity of a solid substance separates, which can be resolved into its components by dissolving it in ether and agitating it with a solution of sodium carbonate. On acidifying the alkaline solution and distilling with steam, benzoic acid passes over, and dihydroxybenzoylbenzoic acid (m. p. about 200°) separates from the contents of the distillation flask on cooling.

The ethereal solution, besides containing traces of resorcinol, consists for the most part of 2 : 4 : 2′ : 4′-tetrahydroxybenzophenone,

$$C_6H_3(OH)_2\cdot CO\cdot C_6H_3(OH)_2,$$

a substance crystallising from hot water in yellow needles melting at 193—195°, and readily giving up water from the hydroxyls in the ortho-position, passing into 3 : 6-*dihydroxyanthone*, $OH\cdot C_6H_3<\!\substack{CO\\O}\!>C_6H_3\cdot OH$ [CO : O : OH = 1 : 2 : 4], which separates in slender needles on adding

water to its alcoholic solution, and decomposes at 300—350°. Its solution in alkali has a strongly marked blue fluorescence.

J. F. T.

Action of Aldehydes on Thiosemicarbazides. By Max Busch and Herm. Ridder (*Ber.*, 1897, **30**, 849—855).—Aldehydes react with thiosemicarbazides in very much the same way as with thiocarbazinic acids (Abstr., 1896, i, 190), yielding thiobiazoline derivatives.

Anilidodiphenylthiobiazoline, $S\left\langle\begin{matrix}CHPh\text{---}NPh\\ \quad\quad\quad\quad\ \ | \\ C(NHPh):N\end{matrix}\right.$. A theoretical yield of the *hydrochloride* is obtained when diphenylthiosemicarbazide and benzaldehyde are mixed with alcohol containing hydrogen chloride in solution. The hydrochloride crystallises in greenish-yellow needles, sinters at 232°, and melts at 240°; it is readily soluble in warm alcohol or acetic acid, but insoluble in cold water, and is decomposed on warming. The *base* is best isolated by decomposing the hydrochloride with dilute ammonia, extracting several times with ether, and then adding light petroleum to the ethereal solution. It crystallises in brownish-red aggregates, and is usually contaminated by a sparingly soluble substance, from which it can be mechanically separated. It melts at 105—106°, and dissolves readily in ether or benzene, yielding dark red solutions. Its alcoholic solution is more orange-red, and on warming yields the above-mentioned sparingly soluble compound, $C_{20}H_{15}N_3S$, which melts and decomposes at 280°.

Anilidophenylmetanitrophenylthiobiazoline hydrochloride, obtained from diphenylthiosemicarbazide and metanitrobenzaldehyde, crystallises in small, intensely yellow needles melting at 203°. The *base* has only been obtained in the form of a red oil.

Anilidophenylstyrylthiobiazoline hydrochloride,

$$S\left\langle\begin{matrix}CH(CH:CHPh)\\ C(NHPh)\text{===}N\end{matrix}\right\rangle NPh,HCl,$$

crystallises in deep yellow needles and melts at 246°.

Anilidophenylmethylthiobiazoline hydrochloride, $S\left\langle\begin{matrix}CHMe\text{------}N\\ \quad\quad\quad\quad\ \ | \\ C(NHPh):N\end{matrix}\right.Ph$, crystallises from its ethereal solution in glistening, long, thin plates, melts at 147°, and is easily reconverted into acetaldehyde and diphenylthiosemicarbazide.

Dibenzylaminophenylnitrophenylthiobiazoline hydrochloride, obtained from phenyldibenzylthiosemicarbazide (see this vol., i, 343) and metanitrobenzaldehyde, crystallises in thin, colourless plates, and melts at 108°.

Pulvermacher has previously shown (Abstr., 1894, i, 304) that alkylthiosemicarbazides of the type $NH_2\cdot NH\cdot CS\cdot NHR$ react with aromatic aldehydes to form benzylidene condensation products $R'CH:N\cdot NH\cdot CS\cdot NHR$.

J. J. S.

Use of Potassium Bismuth Iodide in the Preparation of Organic Bases. By Ernst Jahns (*Arch. Pharm.*, 1897, **235**, 151—156).—The author strongly recommends potassium-bismuth iodide solution for the isolation of alkaloids and other organic bases, such as choline and betaine. The solution as prepared by Kraut (*Annalen*,

1882, **210**, 310) is far more delicate as a reagent than those recommended by Dragendorff and by Mangini (*Gazzetta*, 1882, 155). Narceine, solanine, and veratrine, contrary to Classen's statement, yield precipitates with this reagent, creatinine, many tannins, glucosides, and albuminoid substances also give precipitates. It is, therefore, always advisable to first treat the alkaloidal extracts with lead acetate before adding the potassium-bismuth iodide solution. By means of Kraut's solution, the author has been enabled to detect choline in *flor. chamomill. vulg.*, *herb. millefolii*, *herb. meliloti.*, *fol. malvæ*, *herb. cochleariæ*, *fruct. anisi vulgaris*, *Cort. Sambuci*, and *Sem. robiniæ pseudacaciæ*. Bombelon's *bursine* has also proved to be nothing but choline. Choline, together with small quantities of betaine, have been found in the seeds of *Lathyrus sativus* and of *L. Cicera*. Tables are given showing the relative delicacy of the usual reagents for alkaloids towards different bases (betaine, choline) and towards different plant extracts (*Sem. arecæ*, *fol. millefolii*, &c.). J. J. S.

Homologues of Caffeine. By WILLEM VAN DER SLOOTEN (*Chem. Centr.*, 1896, i, 993—994; from *Diss. Marburg*, 1895, 1—45).—*Ethyltheobromine* (*homocaffeine*), which melts at 164—165°, and is not precipitated from its salts by ammonia, is prepared by heating the silver salt of theobromine with ethylic iodide, or, better, by the action of ethylic iodide on theobromine in presence of alcoholic potash. The aurochloride melts at 226°, the platinochloride above 240°. The author has described and analysed double compounds of ethyltheobromine with mercuric chloride, with mercuric cyanide, and with silver nitrate, and the hydrochloride, hydrobromide, sulphate, acetate, and oxalate. With methylic iodide, an additive product is formed which gives a platinochloride melting at 232°. Ethylic iodide does not form an additive product. Potassium hydroxide converts ethyltheobromine into *homocaffeidinecarboxylic acid*, whose copper salt,

$$(C_9H_{13}N_4O_3)_2Cu,4H_2O,$$

was analysed. By the action of bromine, a mono-substitution product melting at 171—172° is formed, and this, when treated with potassium hydroxide and alcohol, yields an ethoxy-compound, $OEt{\cdot}C_9H_{11}N_4O_2$, melting at 154°. Potassium dichromate and sulphuric acid oxidise ethyltheobromine to carbonic anhydride, methylamine, ammonia, and methylethylparabanic acid, which melts at 44°, and with potassium hydroxide decomposes into oxalic acid and methylethylcarbamide. By oxidation with nitric acid, ethyltheobromine yields methylamine methylethylparabanic acid and a compound melting at 137°. Potassium chlorate and hydrochloric acid at 50° convert ethyltheobromine into monochlorethyltheobromine, which melts at 111°, and a compound analogous to apocaffeine. The latter loses carbonic anhydride when boiled with water, and the solution so formed, on boiling with basic lead acetate, forms lead mesoxalate, a compound analogous to alloxan, but which cannot be reduced to amalic acid, being left in solution.

Propyltheobromine and *isobutyltheobromine* are prepared in a similar way to ethyltheobromine. The former melts at 136°, its platinochloride at above 240°, and its aurochloride at 93°; the latter melts at 129—130°, and its aurochloride at 97°. E. W. W.

Reaction between Herapathite and Barium Carbonate in Dilute Alcohol. By A. CHRISTENSEN (*Zeit. anorg. Chem.*, 1897, **14**, 297—301).—An alcoholic solution of herapathite containing iodine equivalent to 16·65 c.c. N/10 sodium thiosulphate solution, after treatment with barium carbonate, required only 13·55 c.c. of the thiosulphate. The difference in the quantity of iodine is due to a portion of the iodine being reduced by the alcohol whereby hydrogen iodide and acetic acid are formed; the sulphuric acid present was equivalent to 4·3 c.c. of a N/10 solution. For every 4 equivalents of iodine which are converted into hydrogen iodide, 5 equivalents of sulphuric acid are replaced or 5 equivalents of quinine saturated, although at the same time the solution remains neutral. This is effected by the oxidation of the alcohol to acetic acid and 4 atoms of iodine produce 1 molecule of this acid, and 4 molecules of hydriodic acid by which the quinine is saturated. E. C. R.

A Constituent of Cinchona Bark which gives the Reactions of "Digitalinum Verum." By A. BEITTER (*Arch. Pharm.*, 1897, **235**, 137—143).—It is shown that quininotannic acid gives the same reaction with sulphuric acid containing a ferric salt as has already been described by Kiliani (Abstr., 1896, ii, 551) as characteristic of "*digitalinum verum.*" It is therefore necessary, in testing for the latter, to be sure that cinchona bark or its constituents are absent. Extracts from different barks contain very unequal amounts of quininotannic acid, so that this acid not only occurs in different proportions in various barks but also probably occurs in numerous combinations. J. J. S.

Calcium Salt contained in Cinchona Bark and Preparation of Quinic Acid. By JOHAN E. DE VRIJ (*Chem. Centr.*, 1896, i, 937—938; from *Ned. Tydsch. Pharm.*, 1896, 70).—The calcium salt is extracted from the macerated bark, preferably *succirubra*, by cold water until the liquid no longer becomes turbid on heating with ammonium oxalate; exposure to air should be avoided. The extract is evaporated to a syrup in a vacuum and the salt precipitated by adding alcohol; the precipitate is then kneaded with alcohol, dissolved in water, and the cinchona-red which contaminates it removed by boiling the acid solution with magnesia. The author suggests that this plastic calcium salt is derived from an unknown compound formed by the union of quinic acid with quinotannic acid. Quinic acid is prepared from this salt by boiling its solution with a slight excess of calcium hydroxide and evaporating to dryness; during evaporation, the quinotannic acid is converted into cinchona-red, which remains with the lime and calcium quinate. The quinate is extracted with hot water, filtered, crystallised by evaporation, and the pure acid obtained from it by means of oxalic acid. E. W. W.

Strychnine Drugs. By G. SANDER (*Arch. Pharm.*, 1897, **235**, 133—137).—It is shown that the acid known as igasuric acid, which occurs in the officinal strychnine drugs (nux vomica and St. Ignatius' beans) is probably caffetannic acid, since on treatment with potash it yields glucose and dihydroxycinnamic acid (caffeic acid). Keller's method for estimating alkaloids in different drugs is strongly recom-

mended as the best. The author suggests a method for estimating strychnine in the presence of brucine by destroying the brucine with potassium permanganate. The amount of strychnine in the mixed alkaloids from nux vomica varies from 43·9 to 45·6 per cent.; the latter number roughly corresponds with a mixture of strychnine and brucine in molecular proportion. In St. Ignatius' beans, the strychnine varies between 60·7 and 62·8 per cent., the higher number corresponding with 1 mol. of brucine to 2 mols. of strychnine. J. J. S.

Methylation of Hydrotropidine. By RICHARD WILLSTÄTTER *Ber.*, 1897, **30**, 721—728).—The methylation of hydrotropidine by A. W. Hofmann's method proceeds throughout normally, but somewhat differently from the methylation of tropidine. On treatment with freshly precipitated silver oxide and distillation, hydrotropidine methiodide yields *methylhydrotropidine* (dimethyl-Δ^3-tetrahydrobenzylamine), $C_7H_{11}\cdot NMe_2$, a liquid boiling at 189° (corr.), and giving the following salts, namely, a *platinochloride* separating from boiling water in orange-red prisms melting with decomposition at 192—193°; an *aurochloride* consisting of microscopic leaflets melting at 90°; a *methiodide* separating from absolute alcohol in slender needles melting and decomposing at 240°; and an *aurochloride* of the *methiodide* crystallising from dilute alcohol in short prisms melting with effervescence at 135°.

Hydrotropilidene, C_7H_{10}, is formed when an aqueous solution of methylhydrotropidine methiodide is treated with moist silver oxide, and the trimethylamine is removed by distilling the strongly alkaline solution of the methylhydrotropidinemethylammonium hydroxide formed; it is a colourless, highly refractive liquid boiling at 118—119° (120—121° corr.) under a pressure of 715 mm., its sp. gr. = 0·8929 at 0°. It yields an oily *hydrobromide* when treated with an acetic acid solution of hydrobromic acid. J. F. T.

Dihydroecgonidine. By RICHARD WILLSTÄTTER (*Ber.*, 1897, **30**, 702—721).—On reduction with sodium in amylic alcohol solution, anhydroecgonine, or its ethylic salt, passes quantitatively into a saturated compound of the empirical formula $C_9H_{15}NO_2$, for which the author proposes the name dihydroecgonidine.

Dihydroecgonidine is a crystalline compound of neutral reaction closely resembling anhydroecgonine, but somewhat more stable; it gives well-defined crystalline salts with mineral acids. Its ethylic salts are liquids, not decomposed by distillation under diminished pressure. It is inactive, the two asymmetric carbon atoms of anhydroecgonidine having become symmetrical by the saturation of the hydrobenzene ring. From the Merling-Einhorn formula for anhydroecgonine, it must possess the constitution

$$CH\begin{cases} CH_2\cdot NHMe\text{——}O \\ CH_2\text{——}CH_2\text{—}C\cdot \overset{|}{C}O \\ CH_2\text{——}CH_2 \end{cases}$$

When dried in a vacuum over sulphuric acid, dihydroecgonidine contains $\frac{1}{2}H_2O$; this it loses at 105°, and then melts at 200°. The *hydrochloride* crystallises in glistening transparent plates melting at 234—236°, the *platinochloride* in orange-yellow prisms containing $2H_2O$, and the *aurochloride* in yellow scales containing $3H_2O$ and decomposing at 210—212°. The *ethylic*

salt of dihydroecgonidine is a colourless liquid boiling at 137—139° (corr.) at 20 mm., and differing from the ethylic salt of anhydroecgonidine in giving a precipitate with picric acid in concentrated solutions only; the *aurochloride* of this ethylic salt crystallises in glistening, yellow prisms melting at 121—122°, and the *methiodide* in long needles melting at 156°. The *aurochloride* of ethylic dihydroecgonidine methochloride separates from dilute alcohol in scales melting at 168—169°, and the *aurochloride* of dihydroecgonidine from water as a canary-yellow powder containing $4H_2O$, or from concentrated hydrochloric acid as microscopic prisms melting and decomposing at 255°.

Ethylic methyldihydroecgonidine, $NMe{\cdot}C_7H_{10}{\cdot}COOEt$, is best prepared by treating a hot aqueous solution of the methiodide with potassium carbonate; it is a colourless oil boiling at 156° (corr.) under a pressure of 16 mm., and having a strongly alkaline reaction; the *platinochloride* separates from hot water in orange-red, or from alcohol in pale yellow scales melting at 148°. The *methiodide* crystallises from absolute alcohol in flat plates melting at 149—150°, whilst the *aurochloride* of the *methochloride*, obtained by the action of silver chloride and gold chloride on the above, forms small, glistening prisms melting at 153—154°.

Dihydrotropilidenecarboxylic acid, $C_7H_9{\cdot}COOH$, is obtained on treating the methiodide of ethylic methyldihydroecgonidine with caustic soda at 120°; it crystallises from hot alcohol in long, glistening needles melting at 74—75°, and is volatile with steam; the *silver* salt crystallises from water in small needles, and the *tetrabromide* from concentrated formic acid in colourless, glistening scales melting with decomposition at 196—197°. J. F. T.

Arecoline Methiodide. By RICHARD WILLSTÄTTER (*Ber.*, 1897, **30**, 729—730).—The reaction between arecoline and methylic iodide is very violent, and it is necessary to dilute the base with methylic alcohol before adding the iodide.

Arecoline methiodide is a colourless solid, crystallising from absolute alcohol in glistening prisms, and melting at 173—174°; it yields an *aurochloride* which crystallises from methylic alcohol in golden-yellow, rhombic leaflets melting at 134—135°. On fusion with potash, it splits up into dimethylamine and a fatty acid.

Dihydroarecoline methiodide crystallises in nodular masses melting at 155—156°, and the *aurochloride* of the methochloride in glistening flakes melting at 111—112°. J. F. T.

"Scopolaminum Hydrobromicum" and Scopoline. By ERNST SCHMIDT (*Chem. Centr.*, 1896, i, 1199—1200; from *Apoth.-Zeit.*, **11**, 260—262).—According to Hesse (Abstr., 1896, i, 655, and 1897, i, 132), commercial scopolamine hydrobromide consists of a mixture of the hydrobromides of hyoscine and atroscine. The author was unable, however, to isolate either of these bases from the root of *Scopolia* or the seed of *Hyoscyamus*, but obtained scopolamine in considerable quantity (Abstr., 1896, i, 712). Samples of the commercial scopolamine hydrobromide (Merck, Gehe) showed a very varying specific rotatory power ($[\alpha]_D = -25{\cdot}43°, -14{\cdot}58°, -17{\cdot}9°, -6{\cdot}62°$, &c., although identical in other properties. From a strongly lævorotatory aqueous

solution, a nearly inactive scopolamine was obtained by the action of silver oxide. Moreover, from the same *Scopolia* root a hydrobromide of normal and one of very slight rotatory power were isolated, hence the various rotatory powers of the ordinary hydrobromide must be ascribed to the presence of an inactive scopolamine which does not exist in the root, but is formed during the extraction. In respect to physiological action, according to Uhthoff and Axenfeld, there is no difference between the hydrobromides of strong and weak rotatory power. Scopoline, $C_8H_{13}NO_2$, obtained from scopolamine, forms a *monoacetyl* derivative, and with hydriodic acid and amorphous phosphorus yields, in addition to ammonia, methylamine and a hydrocarbon, a hydriodide of a *base*, $C_8H_{15}N$, which is isomeric with hydrotropidine, and very similar to it. Scopoline is scarcely acted on by potassium dichromate and sulphuric acid, but, like tropine, is attacked by barium permanganate, and forms *scopoligenine*, $C_7H_{11}O_2N$, which melts at 205—206°, and gives a *nitroso*-compound, melting at 174—175°. With methylic iodide, scopoligenine re-forms scopoline, which must therefore contain the group NMe. A *methiodide*, $C_8H_{13}NO_2,MeI$, can also be prepared, and this forms an ammonium base which, on distillation, yields *methylscopoline*, $C_8H_{12}MeNO_2$, a compound very similar to methyltropine and boiling at 244°. Methylscopoline unites with methylic iodide to form *methylscopoline methiodide*, $C_8H_{12}MeNO_2,MeI$, and this, on distillation with potassium hydroxide, gives trimethylamine and an unstable substance, $C_7H_8O_2$.

All these reactions of scopoline are in accordance with a composition represented by a formula, $CH_2\left\langle\begin{array}{l} CH_2\text{—}CH_2 \\ CH(OH)\cdot CO \\ CH_2\text{—}NMe \end{array}\right\rangle CH$; this is analogous to Merling's tropine formula, and has been already ascribed to scopoline by Eijkman from measurements of the refractive index.

E. W. W.

Douradinha, or Leaves of Palicourea rigida. By KARL G. SANTESSON (*Arch. Pharm.*, 1897, **235**, 143—150).—The author has obtained a small quantity of an alkaloidal substance from douradinha. It crystallises from its alcoholic solution in colourless needles, or in small prisms and cubes, practically insoluble in water, but readily soluble in alcohol and ether, yielding alkaline solutions. The dried substance sinters at 226—230°, and melts at 235°. With potassium dichromate and concentrated sulphuric acid, the base is coloured yellowish-red, changing rapidly to purple, then to blue-red, and finally to mahogany-brown; vanadin-sulphuric acid causes a deep red coloration, which changes from brown to green. The usual reagents for alkaloids give copious precipitates. A crystalline *sulphate* and a similar *nitrate* have been obtained. The physiological action of the alkaloid on frogs has been studied; it has slight poisonous properties, and causes paralysis of the central nervous system. J. J. S.

Compound of Albumin with Phenol. By M. SHIMADA (*Bull. Coll. Agric. Imp. Univ. Tokyo*, 1897, **2**, 507—509).—*Triphenylalbumin*, $C_{72}H_{109}Ph_3N_{18}SO_{22}$, is formed when finely powdered egg-albumin is heated for some hours on a water bath with phenol (10 parts); it is

precipitated as a flocculent mass by alcohol, and washed with alcohol and water. The compound has no odour or taste, is insoluble in boiling alcohol and water and in aqueous potassium carbonate, readily soluble in hot phenol, and dissolves in 0·5 per cent. caustic potash solution, from which it is precipitated by acetic acid; in strong acetic acid, the substance gradually swells up. It is not attacked by cold hydrochloric acid containing 10 per cent. HCl or by 5 per cent. nitric acid, but 35 per cent. hydrochloric acid gradually dissolves it. The compound gives the biuret and Millon's reaction like ordinary albumin.

Prolonged digestion at 100° with strong hydrochloric acid did not liberate phenol from the compound, and the same negative result, as regards phenol, was obtained after digestion with 30 per cent. sulphuric acid (first at 100° and afterwards on a sand bath). In this experiment, leucine and tyrosine were produced, but the amount of substance was insufficient to decide whether argenine, lysine, and aspartic, glutamic, and phenylamidopropionic acids were formed.

Triphenylalbumin is a good nutrient for micro-organisms, and, like ordinary albumin, is subject to fermentation. N. H. J. M.

Chemical and Physiological Reactions of certain Synthesised Proteid-like Substances. By John W. Pickering (*Proc. Roy. Soc.*, 1897, **60**, 337—349).—The author has prepared a series of colloidal substances from certain derivatives of proteids and other substances.

Fractional heat coagulation shows them to be mixtures of different substances which exhibit different physiological actions. When introduced into the circulation of pigmented rabbits, dogs, or cats, intravascular coagulation of the blood is produced in a similar manner to that with a nucleoproteid. They hasten the coagulation of the blood withdrawn from the carotid, and will, when slowly injected intravenously in minute quantities in dogs, produce a retardation of the coagulability of the intravascular blood.

Colloid α is obtained as a pinkish-grey, friable powder, when equal parts of metamidobenzoic acid and biuret are heated with three times their weight of phosphoric anhydride in a sealed tube at 125°. It dissolves in ammonia, from which, on gentle evaporation, translucent, yellowish plates are obtained readily soluble in warm water. The aqueous solution is neutral, lævorotatory ($\alpha_D = -52$), and does not coagulate on heating; but if a trace of a soluble salt of barium, strontium, calcium, magnesium, or sodium is added, a pronounced coagulum is obtained.

The precipitate formed on the addition of lead acetate resembles a similar precipitate obtained from a proteid solution, in redissolving when hydrogen sulphide is passed through the solution in which it is suspended. The chemical nature of the substance is apparently unchanged, but physiologically its behaviour is quite different, as when injected intravenously into pigmented rabbits or dogs, it does not induce intravascular coagulation.

Colloid β is produced when equal weights of tyrosin, biuret, and twice the weight of phosphorus pentachloride are heated in sealed tubes for 6 hours at from 125—130°. It is a grey powder, insoluble in cold water, and only sparingly soluble on warming; it dissolves

readily in concentrated aqueous ammonia, giving an opalescent lævorotatory solution ($\alpha_D = -48$).

Colloid γ is a sparingly soluble white powder, obtained by heating together in sealed tubes at 130° a mixture of equal weights of alloxan and metamidobenzoic acid with twice their weight of phosphoric anhydride. It dissolves in ammonia, forming an opalescent, straw-coloured solution, which, on evaporation, yields translucent plates; the latter are soluble in water, forming a straw-coloured, opalescent lævorotatory solution ($\alpha_D = -41$). It does not produce intravascular coagulation when intravenously injected into pigmented rabbits, nor does it retard coagulation of blood withdrawn from the carotid.

Colloid δ is formed when equal weights of paramidobenzoic acid and phosphorus pentachloride are heated in sealed tubes at 125° for 3 hours; it is a grey, friable powder insoluble in cold water. From its ammoniacal solution, it is obtained as translucent yellow plates, which dissolve in warm water, forming a straw-coloured, opalescent solution which is lævorotatory ($\alpha_D = -42$).

Colloid ϵ is produced when equal weights of tyrosine and xanthine, and twice their weight of phosphorus pentachloride, are heated in sealed tubes at 125°. It is a yellowish powder, slightly soluble in warm water, and readily in concentrated ammonia; from this solution, on gentle evaporation, it is obtained as translucent, yellow plates, similar to those already described. Its aqueous solution is lævorotatory ($\alpha_D = -38$).

Colloid ζ is prepared in a similar manner to colloid ϵ, hypoxanthine being substituted for xanthine. It resembles the colloid ϵ in all respects, and has a rotatory power of $\alpha_D = -40$.

Colloid η, obtained by the interaction of tyrosine and phosphorus pentachloride, is a pink, friable powder, sparingly soluble in both cold and warm water, but readily in aqueous ammonia. It does not yield any of the distinctive colour reactions of the proteids, and fails to produce intravascular coagulation when intravenously injected into rabbits.

Experiments on the fractional heat coagulation of these synthesised colloids are also described. A. W. C.

Proteose of Wheat. By THOMAS B. OSBORNE (*Amer. Chem. J.*, 1897, **19**, 236—237).—A reply to G. E. Teller (this vol., i, 304).

Organic Chemistry.

Butanes and Octanes in American Petroleum. By CHARLES F. MABERY and EDWARD J. HUDSON (*Amer. Chem. J.*, 1897, **19**, 243—262).—After very careful examination of the lowest fractions obtained from Pennsylvania and Ohio petroleum, the authors conclude that it contains only one butane, namely, isobutane, which is shown by the boiling points of its chloro-derivative, 67—68°, of the corresponding alcohol, 108—109°, and of the sulphide, 172°. This is contrary to what has hitherto been assumed, namely, that the butane is the normal hydrocarbon.

The isobutane is contained principally in the fraction boiling between − 2° and 2°. The chief product of chlorination is the monochloro-derivative (boiling point 67—68°); but, by repeated fractionation, a small amount of a substance distilling fairly constantly at 121—122° was also obtained. This proved to be a dichlorobutane mixed with the monochloro-derivative, but the former was not present in sufficient quantities for complete examination.

Monochloro- and a small amount of a dichloro-pentane were prepared from the fraction of petroleum boiling between 29—30°.

For the examination of the octanes, a portion of Ohio petroleum boiling between 75° and 160° was examined. The octanes were separated exceedingly slowly by fractional distillation, and it was not until after thirty-seven distillations that a large fraction boiling between 118·5—119·5° was obtained. This proved to be an octane yielding a monochloro-derivative boiling at 164—166°.

In addition to this, a second octane was obtained which boiled at 124—125°, and gave a chloro-derivative boiling at 173—174°. Ohio petroleum does not contain an octane with a higher boiling point than 125°, nor any of the following hydrocarbons which have been isolated by various investigators from similar fractions of other petroleums, namely, hexahydromesitylene, di-isobutyl, and isoctonaphthene.

A. W. C.

Di-iodacetylene and Tetriodethylene. By HEINRICH BILTZ [with STEPHAN WERNER] (*Ber.*, 1897, **30**, 1200—1210).—A mixture of di-iodacetylene and tetriodethylene is formed by the action of iodine dissolved in potassium iodide solution on calcium carbide, the product being free from di-iodethylene. This substance was described by Maquenne (Abstr., 1893, i, 449) as di-iodacetylene, a similar mixture having also been obtained by Berend (*Annalen*, 1865, **135**, 257). Pure di-iodacetylene is obtained by distilling this mixture with water vapour at 100 mm. pressure, or with acetic acid, the pure substance passing over into the distillate. It crystallises in small, colourless, brittle needles melting at 78°, has a repulsive odour and volatilises very readily, its vapour attacking the mucous membrane violently.

Tetriodethylene has previously been described by Maquenne and

Taine (*Apoth. Zeitung*, 1893, **8**, 613). It is non-volatile and odourless and melts at 187°.

Di-iodacetylene yields tetriodethylene when it is dissolved in water and heated at 100° (Meyer and Pemsel, Abstr., 1896, i, 517), when it is exposed to light, or when it is dissolved in alcohol and concentrated sulphuric acid added to the solution.

Both di-iodacetylene and tetriodethylene are converted by chlorine into hexachlorethane, and by bromine into hexabromethane.

When di-iodacetylene is treated in ethereal solution with nitrous fumes (from nitric acid and arsenious oxide), it yields *nitrotri-iodethylene*, $CI_2{:}CI{\cdot}NO_2$, which crystallises in lemon-yellow, silky needles, and melts at 107°. A better yield is obtained when an ethereal solution of iodine is added. The compound is not decomposed when heated with alcoholic potash or alcoholic sulphuric acid.

An unstable substance, which was probably an impure form of this compound, was described by Berend (*loc. cit.*). A. H.

Sodium Carbide and Monosodacetylene. By CAMILLE MATIGNON. (*Compt. rend.*, 1897, **124**, 775—777).—Between its melting point and 190°, sodium decomposes acetylene with production of monosodacetylene, C_2HNa. Above 210°, sodium carbide, C_2Na_2, is formed, whilst beyond 210—220°, monosodacetylene decomposes into acetylene and sodium carbide, and at the same temperatures sodium acts on monosodacetylene, with liberation of hydrogen and formation of sodium carbide. All these reactions are quantitative, and the products are white solids. It is, however, essential to constantly agitate the sodium in order to prevent too great local rises of temperature with consequent separation of carbon. The sodium is best contained in a flask which is heated in an oil bath, and the acetylene must be carefully dried. C. H. B.

Ammonium Cyanide and its Manufacture. By DENIS LANCE (*Compt. rend.*, 1897, **124**, 819—821).—When ammonia is passed slowly over wood charcoal heated at 1000—1100°, ammonium cyanide is always formed, contrary to the statement of Bueb and Bergmann. The yield of cyanide is at a maximum at this temperature, and 25 per cent. of the nitrogen in the ammonia is converted into cyanogen. This yield is, however, greatly increased if the ammonia is mixed with nitrogen and hydrogen, especially when the latter is in excess, and the yield of cyanogen may be nearly 90 per cent. of the ammonia when 200 c.c. of ammonia is mixed with 5000 c.c. of hydrogen and 500 c.c. of nitrogen. Under these latter conditions, at least 70 per cent. of the nitrogen in the ammonium cyanide is derived from the free nitrogen in the gaseous mixture. C. H. B.

Hydrocobaltocobalticyanic Acid and its Salts. By C. LORING JACKSON and ARTHUR M. COMEY (*Amer. Chem. J.*, 1897, **19**, 271—281). —When potassium cobalticyanide is boiled with strong nitric acid, the mixture gradually turns red, the colour increasing with prolonged boiling, and after a time the whole is converted into a semi-solid, gelatinous mass. The product is purified by heating with nitric acid and then washing with water; the insoluble jelly thus obtained is dried in a vacuum, when it changes in colour from red to a greyish

green. It is very hygroscopic, absorbing water from the air rapidly and regaining its red colour. Analysis shows that the substance has the composition $KH_2Co_3(CN)_{11}H_2O$; and it is, therefore, *monopotassium cobaltocobalticyanide.* The crude product is insoluble in cold water, and nearly so in hot water, but after the impurities are washed out it dissolves slowly. The solution has a strong acid reaction, and gives precipitates with salts of many of the heavy metals.

When a solution of the monopotassium compound is treated with excess of potash, it turns dark brown, and, on boiling, a black precipitate of cobaltic hydrate is thrown down. If the boiling is continued until no more precipitation takes place, the liquid filtered, and the light yellow filtrate acidified with acetic acid and precipitated with alcohol, white needles are obtained, which prove to be potassium cobalticyanide. This salt generally crystallises in broad, rhombic crystals, the form in which it here appears being due, in all probability, to a small amount of impurity.

The *dipotassium, barium, silver, copper*, and *zinc* salts of cobaltocobalticyanic acid are also described. A. W. C.

Action of Mercuric Chloride on Alcohols. By FONZES-DIACON (*Bull. Soc. Chim.*, 1897, [iii], **15**, 762—763).—Alcohols are oxidised when boiled with mercuric chloride, with formation of aldehydes and precipitation of mercurous chloride. In the case of a solution of mannitol, the reaction was found to be particularly rapid.

M. W. T.

Constitution of Phosphorous Acid. By C. A. AUGUST MICHAELIS and THEODOR BECKER (*Ber.*, 1897, **30**, 1003—1009).—The constitution of phosphorous acid (*Annalen*, 1876, **181**, 312) has not hitherto been definitely settled, since the various reactions in which it takes part can all be interpreted, both by the symmetric formula, $P(OH)_3$, and the asymmetric formula, $PHO(OH)_2$. The author has now succeeded in obtaining further evidence in favour of the latter of these.

When lead phosphite, $PbHPO_3$, is treated with ethylic iodide at 175°, it yields the diethylic phosphite, $PHO(OEt)_2$, which was obtained by Thorpe and North by the action of phosphorous anhydride on alcohol (Trans., 1890, 634). When this compound is treated in ethereal solution with sodium, and then with ethylic iodide, it yields *diethylic ethylphosphinite*, $PEtO(OEt)_2$, which is isomeric with ethylic phosphite, $P(OEt)_3$, and differs from it in all its properties. Thus, it boils at 198°, has a sp. gr. = 1·025 at 21°, and in aqueous solution does not reduce mercuric chloride or precipitate magnesium mixture, whereas ethylic phosphite reduces mercuric chloride, boils at 191°, and has a sp. gr. = 1·075.

Diethylic ethylphosphinite is also formed when *ethyloxychlorophosphine*, $PEtOCl_2$, which is prepared by the action of sulphurous anhydride on ethylchlorophosphine, and boils at 175—178°, is treated with sodium ethoxide.

Ethylphosphinous acid, therefore, stands in the same relation to phosphorous acid as ethylsulphonic acid to sulphurous acid. A. H.

Molecular Modifications and Multirotation of the Sugars. By CHARLES TANRET (*Bull. Soc. Chim.*, 1896, [iii], **15**, 195—205, and

349—361).—The author has shown that, in the case of glucose and in that of isodulcitol (Abstr., 1895, i, 490; 1896, i, 334), the multirotation of the sugar solutions is due to a transformation of one modification into another under the influence of water. *Galactose*, like glucose, exists in three modifications. The ordinary or α-galactose, when freshly dissolved in water, has a rotatory power $[\alpha]_D = +135°$. The rotatory power diminishes when the solution is left to itself, or more rapidly when the solution is boiled, and at length attains a value of $[\alpha]_D = +81·6°$. The galactose is then completely converted into the β modification. But if galactose is dissolved in hot alcohol, its rotatory power is reduced eventually to $[\alpha]_D = +53°$, and it is converted into a new or γ modification. Both the β and γ modifications can be obtained in solid condition by crystallisation from mixtures of alcohol and water. *Arabinose* forms two modifications. When first dissolved in water, the ordinary or α form has a value $[\alpha]_D = +175°$. This changes, however, gradually, and falls to $[\alpha]_D = +104—105°$. The α has then been converted into the β modification. β-Arabinose can be obtained by precipitating arabinose from its cold aqueous solutions by means of alcohol. *Xylose* behaves like arabinose, the rotatory power in aqueous solution falling from $[\alpha]_D = +78°$ to $[\alpha]_D = +18·9°$. Pure crystals of β-xylose could not be obtained. *Milk-sugar*, like glucose and galactose, exists in three modifications. The α form has the rotation $[\alpha]_D = +92·6°$, and crystallises out from cold, aqueous solutions of milk-sugar. The β modification, $[\alpha]_D = +56°$, is formed when the crystallisation takes place at 85—86°. The γ form is produced by precipitating milk-sugar from the aqueous solutions with alcohol. Its rotation is $[\alpha]_D = +34·5°$.

Each modification of a sugar has then its own rotatory power, and it appears, therefore, that the multirotation of the reducing sugars is due to the transformation of one modification into another in aqueous solution. H. C.

Chemistry of Honey. By O. KÜNNMANN and ALBERT HILGER (*Chem. Centr.*, 1896, ii, 476—478; from *Forsch.-Ber. Lebensm. u. Bez. Hygiene*, &c., 3, 211—226).—Lævorotatory honeys contain only traces of dextrins, whilst in all dextrorotatory forest honeys they are present in greater quantity and bear a direct relation to the rotatory power. Hence honeys of the former class, on fermentation with large amounts of yeast, easily produce an inactive residue after fermentation. Von Raumer and Mader have shown that pressed yeast acts more strongly on honey dextrin than beer-yeast, hence Sieben, who always used the former, invariably obtained inactive residues from pure honeys, and regarded honeys which yielded dextrorotatory residues as adulterated. In order to obtain an exact comparison of the powers of fermentation of the various yeasts, the authors experimented with a dextrin which had been carefully isolated from dextrorotatory honey. Solutions were prepared containing the other necessary components of honey in their natural proportions. Fermentation was carried on at 25° for 140 hours in flasks charged with 150 c.c. of solution, with 10 grams of yeast, and closed by cotton-wool plugs. Three beer yeasts from different breweries, freed from wort by water, yielded slightly dextrorotatory residues. Two pressed yeasts from different sources produced inactive

residues. Pressed yeasts always contain schizomycetes. A species of yeast obtained from pressed yeasts by pure cultivation and free from schizomycetes gave a far less energetic fermentation and left a dextrorotatory residue. Wine yeasts were incapable of fermenting honey-dextrin; in 16 to 20 days, only 8·7 to 13·1 per cent. of dextrin was attacked. Beer yeasts worked more actively, but the *Saccharomyces Pombe* from Africa was the only one which effected complete fermentation; in other cases, only from about 25 to 40 per cent. was fermented. The last portions of invert-sugar are only attacked after prolonged fermentation. In many cases, after employing the osazone test, a flocculent, yellow mass separated from the cooled filtrate from the glucosazone, but its quantity was insufficient to allow of examination.

Larger quantities of honey-dextrin were obtained by repeated precipitation by alcohol, and removal of diffusable substances by dialysis, &c., the liquid being finally treated with ether and alcohol, and the precipitate dried. It forms a snow-white, almost tasteless, amorphous powder, easily soluble in water, contains 0·3 to 0·5 per cent. of ash, and is far less hygroscopic than the product obtained before dialysing. Its aqueous solution is neutral, reduces Fehling's solution on boiling; the filtrate after inversion of the sugar by hydrochloric acid is again capable of reducing Fehling's solution, and possesses a rotatory power of about half its original value. Large quantities of glucosazone were obtained by means of phenylhydrazine from the neutralised inverted solution. A dilute solution of iodine in potassium iodide does not produce a coloration, hence achroodextrin with only the slightest traces of erythrodextrin can be present, and none of the latter could be obtained by fractionation with 75 per cent. alcohol. As a preliminary proof of the presence of a disaccharide, the phenylhydrazine test was employed and an osazone melting at 145—147° and evolving gas at 178° was obtained. Isomaltosazone melts at 153—155°. As Ost, Brown and Morris and Jalowetz have shown, however, that phenylhydrazine in presence of dextrin does not give a pure maltosazone, the authors repeated Ost's experiments and found that a variety of osazones melting between 145° and 175° were obtained by varying the proportions of dextrin and maltose. The honey-dextrin was, therefore, treated by Lintner and Düll's method, namely, fractionating a 20 per cent. solution with 90 per cent. alcohol, and then with 85 per cent. alcohol, until the reducing power was 18 (maltose = 100). Finally, fractionation of a 10 per cent. solution with 80 per cent. alcohol was carried on until phenylhydrazine gave no osazone, and the product then dialysed until it was free from ash. The solution remaining on the membrane was evaporated in a vacuum, dissolved in 2 parts of water, and precipitated by alcohol and ether. On reprecipitating from a 10 per cent. solution by 80 per cent. alcohol, both precipitate and filtrate showed the same specific rotatory power $[\alpha]_D = +191°$, and a reducing power = 10. Hence this dextrin is identical with Lintner's achroodextrin obtained by means of diastase, and with Mittelmeier's achroodextrin isolated from beer wort. It could not be obtained in a crystalline form, but its molecular weight, as determined by the freezing point method, was 1926, which corresponds approximately with the formula $(C_{10}H_{20}O_{10})_6 + H_2O$.

All the fractions obtained in the preparation of the dextrin possessing a rotatory power of less than 145° were mixed and evaporated in a vacuum. Finally, by mixing all the solutions of a rotatory power of from about +140° to +145° and precipitating from a 20 per cent. solution by 90 per cent. alcohol, a substance of rotatory power = +140·8° was obtained. By precipitating from a 30 per cent. solution in methylic alcohol by gradual addition of absolute alcohol, its rotatory power was reduced to 140°, and after dialysing three times, allowing four-fifths of the solution to pass through the membrane, the rotatory power of the residue was +159°, and that of the solution which had passed through 139°. From the latter, a light yellow osazone, crystallising in small needle clusters, was obtained. After drying over sulphuric acid, it had a specific rotatory power $[\alpha]_D$ = +54°, and after drying at 100°, melted at 184—186°. This disaccharide is probably maltose, although maltosazone has a specific rotatory power $[\alpha]_D$ = +61°, and melts at 202—206°.

In the separation of achroodextrin from dextrorotatory honey by dialysis, it was found that, by prolonging the process, an achroodextrin containing maltose remained on the membrane ($[\alpha]_D$ = +187·5°, reducing power = 15·9), and the solution outside the membrane ($[\alpha]_D$ = +161°) contained small quantities of achroodextrin.

E. W. W.

Preparation of Primary Amines. By MARCEL DELÉPINE (*Compt. rend.*, 1897, **124**, 292—295).—In a previous communication (Abstr., 1895, i, 326), the author has shown that when hexamethylenetetramine alkyliodides are boiled with dilute hydrochloric acid, they are hydrolysed in accordance with the equation $C_6H_{12}N_4RI + 6H_2O = 6CH_2O + 3NH_3 + NRH_3I$. In alcoholic solution, these reactions occur more readily, owing partly to the development of energy due to the formation of methylene diethoxide by the interaction of the formaldehyde with the alcohol. The equation then becomes $C_6H_{12}N_4RR' + 3HCl + 12C_2H_6O = 6CH_2(OEt)_2 + 3NH_4Cl + NRH_2HR'$, R representing the alkyl group and R′ the halogen. For the preparation of allylamine, one molecular proportion of allylic iodide is added to a mixture of hexamethylene tetramine with four times its weight of chloroform. On warming, the reaction proceeds rapidly. The crystalline double salt, $C_6H_{12}N_4,C_3H_5I$, is separated and dissolved in a mixture of 95 per cent. alcohol and aqueous hydrochloric acid (sp. gr. 1·33) in the proportions demanded by the above general equation. On gently warming, the reaction occurs and the liquid separates into two layers, the upper one consisting of methylene diethoxide, the lower one containing the ammonium chloride and the salt of the amine partly in solution and partly in the solid state. The methylene diethoxide is distilled off, and the residue twice treated with a further quantity of alcohol and acid, in order to decompose the intermediate methylenic compound of the amine which is formed. After distillation and treatment of the residue with a caustic alkali, the amine is easily obtained. By substituting benzylic chloride for the allylic iodide in the above preparation, benzylamine is readily prepared, 70 grams of hexamethylenetetramine and 70 grams of benzylic chloride yielding 45 grams of the pure amine. A. C. C.

Preparation of Allylamine. By SIEGMUND GABRIEL and GEORG ESCHENBACH (*Ber.*, 1897, **30**, 1124—1125).—The authors recommend the use of hydrochloric acid instead of sulphuric in Hofmann's method for the preparation of allylamine (*Ber.*, 1868, **1**, 183). Allythiocarbimide (50 grams) is boiled with 20 per cent. hydrochloric acid (200 c.c.) until the oil is completely dissolved, an operation which requires some 5 hours. The mixture is evaporated on the water bath, the crystalline mass dissolved in as little water as possible, then decomposed with caustic potash, and the oily base separated. The yield is about 76 per cent. of the theoretical. J. J. S.

Thionyl Derivatives of the Aliphatic Diamines. By C. A. AUGUST MICHAELIS and PAUL GRAENTZ (*Ber.*, 1897, **30**, 1009—1014. Compare Abstr., 1893, i, 504).—Ethylenediamine reacts with thionyl chloride to form *dithionylethylenediamine*, $SO:N\cdot CH_2\cdot CH_2\cdot N:SO$, which is a pale yellow, viscid liquid of characteristic penetrating odour, solidifies at 5·5° and boils at 100° (pressure = 25 mm.); it decomposes gradually when preserved, and is also readily decomposed by water. Ethylenediamine also reacts with thionylaniline to form an unstable yellow product. When ethylenediamine is suspended in ether and treated with sulphurous anhydride, an unstable compound is formed which passes by loss of sulphurous anhydride into the *compound*, $\begin{matrix} CH_2\cdot NH_3 \\ | \\ CH_2\cdot NH \end{matrix}\!\!>\!SO_2$, which is probably an internal salt of ethylenethionamic acid, and is a white, very hygroscopic mass, which decomposes when heated. More stable products are formed by the action of aldehydes on the ethylenethionamic acid. When benzaldehyde is added to an alcoholic solution of ethylenediamine saturated with sulphurous anhydride, *benzaldehyde-ethylenethionamic acid*,

$$NH_2\cdot C_2H_4\cdot N(SO_2H)\cdot CHPh\cdot OH,$$

is formed, which crystallises in small, white plates and melts at 169°.

Salicylaldehyde-ethylenethionamic acid is a pale yellow, hygroscopic, crystalline powder, which decomposes when heated.

Anisaldehyde-ethylenethionamic acid forms small, white needles melting at 166°. The *cinnamaldehyde* compound melts and decomposes at 165°. Furfuraldehyde also yields a *compound*, which forms stellate aggregates of brown needles, melting at 153°.

Dithionyltrimethylenediamine, $SO:N\cdot CH_2\cdot CH_2\cdot CH_2\cdot N:SO$, is a golden-yellow liquid which boils at 117° (pressure = 26 mm.). *Benzaldehyde-trimethylenethionamic acid* melts at 102°; the *salicylaldehyde* compound is a lemon-yellow, hygroscopic powder, melting at 104°; the *anisaldehyde*, *cinnamaldehyde*, and *furfuraldehyde* compounds are all hygroscopic and decompose on melting. A. H.

Action of Ethers on Phosphonium Iodide. By PETER FIREMAN (*Ber.*, 1897, **30**, 1088—1090).—Methylic and ethylic ether react with phosphonium iodide in the same manner as the corresponding alcohols, the tertiary base and quaternary iodide being produced, but no primary or secondary base being formed. The reaction, however, proceeds at a lower temperature when the ethers are employed, probably on account

of the fact that only half as much water is produced in the reaction with the ethers as in that with the alcohols. A. H.

Condensation-products of Isovaleraldehyde. II. By LEOPOLD KOHN (*Monatsh.*, 1897, **18**, 189—198. Compare Abstr., 1896, i, 10, 461).—When isovaleraldehyde is mixed with a very little solid potassium hydroxide, the mixture at once cooled and kept cool until the reaction is over, the product treated with water, saturated with carbonic anhydride, and the oil washed with water, a quantitative conversion of isovaleraldehyde into *isovaleraldol*,

$$CH_2Pr^{\beta}\cdot CH(OH)\cdot CHPr^{\beta}\cdot CHO,$$

is realised. This substance boils at 120° under 18 mm. pressure; it can sometimes be distilled unchanged, but at other times it will decompose into isovaleraldehyde. When distilled under atmospheric pressure, it loses water and yields an unsaturated aldehyde, *isopropylisobutylacraldehyde*, $CH_2Pr^{\beta}\cdot CH\colon CPr^{\beta}\cdot CHO$, and the same reaction occurs when an attempt is made to prepare an acetyl derivative, or to reduce it to a glycol. It can, however, be oxidised with potassium permanganate to an *acid*, $CH_2Pr^{\beta}\cdot CH(OH)\cdot CHPr^{\beta}\cdot COOH$, which melts at 56°, but has a great tendency to form a syrup which crystallises with difficulty; the acid, melting at 120°, to which Wohlbruck (Abstr, 1888, 1099) assigned the same constitution, must be differently constituted. By the action of hydroxylamine on the aldol, the *oxime* was obtained, together with those of valeral and of the acraldehyde; it boils at 169° under 25 mm. pressure, but it tends to lose water when distilled, or when treated with acetic anhydride; in the first case, the oxime of the acraldehyde is formed, in the second, the nitrile of the acid $C_{10}H_{18}O_2$.
C. F. B.

Fatty Ketones of High Molecular Weight. By JOSEPH BERTRAND (*Bull. Soc. Chim.*, 1897, [iii], **15**, 764—768).—*Ethyl pentadecyl ketone* is formed by the action of palmitic chloride on zinc ethyl in ethereal solution, and subsequent treatment of the product with water; it is a white, crystalline substance which melts at 53°, boils at 197·5° under 11 mm. pressure, and is soluble in alcohol, ether, and light petroleum, but insoluble in water. Immediately after distillation, it melts at 50·5°, but after a time the substance undergoes some physical change, and its melting point rises to 53°. *Propyl pentadecyl ketone*, obtained by the action of palmitic chloride on zinc propyl in ethereal solution, is a white substance which immediately after distillation melts at 48°, but after some time at 50·5°; it distils without much decomposition at 211° under 11 mm. pressure, is insoluble in water, but soluble in alcohol, ether, and light petroleum, and when oxidised with chromic acid mixture, yields pentadecoic acid, melting at 51°. Both these ketones give oximes with hydroxylamine hydrochloride, and unstable hydrazones with phenylhydrazine. *Ethyl pentadecyl ketoxime* is a white solid, soluble in alcohol and ether, but insoluble in water; it softens at 42°, melts at 44°, and boils without decomposition. *Propyl pentadecyl ketoxime* melts at 28°. M. W. T.

Conversion of Oleic Acid into Stearolactone and Hydroxystearic Acid. By DAVID (*Compt. rend.* 1897, **124**, 466—468).—If

ice-cold water is added to a mixture of oleic acid and monhydrated sulphuric acid in molecular proportion, care being taken to avoid any rise of temperature, the liquid separates into two layers, the lower one consisting of dilute sulphuric acid, the upper one of a mixture in equal proportions of a sulpho-acid not decomposed by cold water and hydroxystearic acid. Approximately one-half of the sulphuric acid originally employed is always found in the lower layer.

If this dilute acid is separated and an equal volume of cold water added to the remaining oil, it dissolves completely, and the solution, on standing for 12 hours at a temperature of 4°, deposits crystals of stearolactone in quantity corresponding with 18—20 per cent. of the oleic acid taken. The filtrate from the lactone, when boiled for 1 hour and allowed to stand, deposits crystals of hydroxystearic acid melting at about 80° and solidifying at 68°. If, instead of boiling the filtrate from the lactone, it is kept at a temperature of 4° or 5° for a sufficiently long time, the whole of the hydroxystearic acid will undergo conversion into stearolactone which can be separated in the crystalline state. The author is of opinion that the α-hydroxystearic acid, $C_{14}H_{29}\cdot CH_2\cdot CH_2\cdot CH(OH)\cdot COOH$, formed in the above reaction undergoes slow conversion in the cold into the γ-acid,

$$C_{14}H_{29}\cdot CH(OH)\cdot CH_2\cdot CH_2\cdot COOH,$$

which in turn furnishes the lactone. From 100 parts of oleic acid, 50 parts of solid products can be thus obtained. A. C. C.

Hazel-nut Oil. By A. SCHÖTTLER (*Chem. Centr.*, 1896, ii, 417; from *Apoth. Zeit.*, 11, 533—534).—The oil obtained by pressing (50—55 per cent. yield) has a sp. gr. = 0·916 at 15°, Hübl's iodine number = 87, saponification number = 187, Hehner's number = 95·5, Reichert-Meissl number = 0·99 and the refractive index as determined in the butter refractometer is 1·468—1·478. The melting point of the fatty acids is 19—20°. Saponification shows that this oil contains chiefly glycerides of oleic acid with only very small quantities of palmitic acid, hence it is very similar to almond oil. E. W. W.

Action of Ammonia and Amines on Ethylic Oxalacetate. By WILHELM WISLICENUS and WALTER BECKH (*Annalen*, 1897, 295, 339—366. Compare Abstr., 1895, i, 335).—Ammonia combines with ethylic oxalacetate, yielding an additive compound (*loc. cit.*); it is now found that primary and secondary bases exhibit the same behaviour, whilst tertiary amines condense with two molecular proportions of the salt without forming an additive compound. The additive compound of ammonia with ethylic oxalacetate readily decomposes forming a substance which has been hitherto regarded as ammonium triethylic aconitoxalate (compare Claisen and Hori, Abstr., 1891, 424); its behaviour, however, is more in accordance with the formula

$$\left.\begin{array}{l} CO\text{————}O \\ \mid \\ CO\cdot CH(COOEt) \end{array}\right> C \left< \begin{array}{l} COOEt \\ CH_2\cdot COOEt \end{array}\right.$$

and the authors therefore propose, with the concurrence of Claisen, to refer to this substance as ethylic oxalocitrolactone. The additive compounds of ethylic oxalacetate with primary and secondary amines undergo condensation on the lines of the ammonia compound, and it is

noteworthy that, in the case of tertiary bases, no intermediate production of an additive compound is noticeable.

The compound of ethylic oxalacetate with ammonia develops an intense red coloration with ferric chloride; copper acetate precipitates the copper derivative of ethylic oxalacetate, whilst barium chloride gives rise to the *barium* derivative, which crystallises from hot alcohol, and melts indefinitely at 205°. Ammonium ethylic oxalocitrolactone (Abstr., 1895, 335) has been already described as arising from the foregoing compound on fusion.

Ethylic oxalocitrolactone, $\begin{matrix}CO\text{---------}O \\ | \\ CO\cdot CH(COOEt)\end{matrix}\!\!>C<\!\!\begin{matrix}COOEt \\ CH_2\cdot COOEt\end{matrix}$, melts and decomposes at 213—215°, and is identical with the ethylic aconitoxalate of Claisen and Hori; it is produced on acidifying the ammonium compound, and also by the action of sodium ethoxide on ethylic oxalacetate. The *sodium* derivative develops a deep red coloration with ferric chloride.

Ethylic oxalacetate and ethylamine form an *additive compound*, which crystallises from alcohol in long, colourless needles, and melts at 107°; ferric chloride develops an intense red coloration with the aqueous solution, and copper sulphate precipitates the copper derivative of ethylic oxalacetate. On boiling the alcoholic solution, the *ethylamine* compound of ethylic oxalocitrolactone is obtained as a yellowish-brown syrup which does not solidify.

The *additive compound* of diethylamine and ethylic oxalacetate melts at 109°, and undergoes no spontaneous change; the alcoholic solution, however, when boiled, yields the *diethylamine* compound of ethylic oxalocitrolactone, which crystallises from a mixture of alcohol and ether, and melts at 126°.

Piperidine combines with ethylic oxalacetate, and the *additive compound*, which melts at 74°, is most conveniently purified by treatment with ether on porous earthenware; the *piperidine* compound of ethylic oxalocitrolactone is produced by the spontaneous change of the foregoing substance, and melts at 93°.

When trimethylamine is passed into an ethereal solution of ethylic oxalacetate at −10°, the *trimethylamine* compound of ethylic oxalocitrolactone separates as an oil; the *triethylamine* compound is crystalline, and melts at 64°, and the *pyridine* compound at 83°. Triethylamine also precipitates a crystalline compound from an ethereal solution of ethylic dioxalosuccinolactone; it dissolves in water, and melts at 80—82°.

Benzylamine and ethylic oxalacetate combine to form an *additive compound* which melts at 88°; its behaviour, however, differs from that of the compounds already considered, as in a short time it becomes converted into dibenzyloxamide, which melts at 218°, along with the *benzylamine* salt of benzylamido-oxalic acid,

$$CH_2Ph\cdot NH\cdot CO\cdot COO\cdot NH_3\cdot CH_2Ph,$$

which crystallises from alcohol in white needles, and melts at 164°.

The *lactone*, $C_6H_4<\!\!\begin{matrix}O\text{—}CO \\ \quad\;\; | \\ N : C\cdot CH_2\cdot COOEt\end{matrix}$, is obtained from orthamidophenol and ethylic oxalacetate, and crystallises in slender needles

melting at 102°; it is easily resolved into its components by alcoholic soda, and does not develop any colour with ferric chloride.

M. O. F.

Polymethacrylic Acid. By J. ALFRED MJÖEN (*Ber.*, 1897, **30**, 1227—1240. Compare *Annalen*, 1877, **188**, 47).—The polmeride of methacrylic acid, which is formed when the latter is preserved either alone or in presence of a drop of acid, can be obtained in the anhydrous state, as a white powder, by dissolving it in alcohol and precipitating with ether. It possesses many of the properties of the colloids, and swells up before dissolving in water. It also dissolves in concentrated sulphuric acid, and is not oxidised by fuming nitric acid, potassium permanganate, or potassium dichromate. It readily dissolves in aqueous potash, requiring 1 mol. of potash for each group of the composition $C_4H_6O_2$ which is present, so that if its formula be taken as $(C_4H_6O_2)_n$ it is *n*-basic. When heated, it begins to decompose at 200°, and volatilises at 300° without melting; it cannot be distilled, even in a vacuum, without undergoing complete decomposition. The determination of its molecular weight by the boiling point method, the freezing point method, and by the increase in conductivity on dilution, although not affording very consistent results, seems to point to some value in the neighbourhood of 8 for *n*. This result is to some extent confirmed by the fact that when the acid is titrated with baryta water, the precipitate which is formed as each drop of the alkaline solution is added at once redissolves until 2 equivalents of baryta (calculated from the simple formula $C_4H_6O_2$) have been added; after this point, the precipitate remains undissolved and the liquid becomes neutral when 8 equivalents of baryta are present. The author therefore concludes that the acid is octobasic, having the formula $C_{24}H_{40}(COOH)_8$, and forms an acid salt in which two of the hydrogen atoms have been replaced by barium. The other salts of the acid, except those of the alkali metals, form gelatinous masses. The acid itself diffuses slowly through parchment paper.

A. H.

Constitution of the Acid Amides. By WILHELM ESCHWEILER (*Ber.*, 1897, **30**, 998—1003).—When glycollic nitrile is heated with water at 130°, nitriloacetonitrile and glycollic acid are formed together with two substances, one of which melts at 55°, whilst the other melts and decomposes at 161°. The last of these has the composition $C_2H_5NO_2$, and is therefore isomeric with glycollamide, and, like this substance, yields calcium glycollate when it is heated with milk of lime. The same compound was obtained from ethylglycollimide. It differs from glycollamide, which melts without decomposition at 115—120°, in being sparingly soluble in alcohol, and in yielding a white precipitate of calcium glycollate when calcium chloride is added to its aqueous solutions.

It appears probable that this new compound represents the imido-form, $OH\cdot CH_2\cdot C(OH)\!:\!NH$, corresponding with glycollamide,

$$OH\cdot CH_2\cdot CO\cdot NH_2.$$

A. H.

Acidyl Amides. By ARTHUR R. HANTZSCH (*Annalen*, 1897, **296**, 84—94. Compare Lachmann, Abstr., 1896, i, 601).—The existence of two classes of nitro-compounds having the formulæ $R\cdot CH_2\cdot NO_2$

and $R\cdot CH<\overset{N\cdot OH}{\underset{O}{|}}$, has been already indicated by the author (Abstr., 1896, i, 672), and an attempt is now made to apply a similar classification to the metallic derivatives of acidyl amides; according to such a scheme, these compounds would be regarded as derived from a normal amide, $R\cdot CO\cdot NH_2$, or an iso-amide, $R\cdot C(OH)\colon NH$, the corresponding thiocarbamides being expressed by the formulæ $NH_2\cdot CS\cdot NH_2$ and $NH\cdot_2C(SH)\colon NH$.

Although it has not been found possible to isolate two modifications of amides, the author is of opinion that there is sufficient evidence to justify the metallic derivatives of amides and urethane being regarded as having the metal united with oxygen; this generalisation fails, however, in the case of the mercury derivatives, it being found that the mercury derivative of acetamide has a more feeble electrical conductivity than mercuric chloride, and mercuric oxide, moreover, does not separate from an aqueous solution of the substance.

A comparison is instituted between acidyl amides and nitramide, it being shown that, whilst the former substances are neutral, exhibit feeble electrical conductivity, and do not combine directly with ammonia, nitramide has an acidic action, conducts electricity, and forms a solid ammonium derivative; this is regarded as evidence against the presence of the NH_2 group in nitramide. M. O. F.

A Higher Homologue of Carbamide. By W. Oechsner de Coninck (*Compt. rend.*, 1897, **124**, 200—201).—From the urine of a patient suffering from alcoholism, the author has isolated a compound having the formula $C_4H_{10}N_2O$, which he regards as the fourth member of a homologous series commencing with carbamide. The syrupy urine is treated with 98 per cent. alcohol and filtered. The residue, after the evaporation of the alcohol, is acidified with hydrochloric acid and extracted with ether. The liquid, after neutralisation with ammonia, is treated with basic lead acetate and filtered, the excess of lead being removed from the filtrate by sulphuretted hydrogen. The filtrate from the lead sulphide, after evaporation to a syrupy consistency and extraction with absolute alcohol, consists of yellow crystals which are decolorised by means of animal charcoal. The colourless crystals thus obtained, when dried in a vacuum, melt at 270°, undergoing decomposition, and are soluble in hot water, slightly soluble in cold water and dilute alcohol, and insoluble in strong alcohol. This compound combines with acids and with metallic oxides, and undergoes decomposition with disengagement of nitrogen when heated with alkaline solutions of sodium hypochlorite. Baumstarck, in 1873, separated from the urine of an icteric patient a compound having the formula $C_3H_8N_2O$, which he regarded as the third member of the series above referred to. It is suggested that, in proportion as the oxidising power of the organism is weakened, the molecular weight of the compounds eliminated by the kidneys increases.

A. C. C.

Remarks on Zelinsky's "Researches in the Hexamethylene Series." By Wladimir B. Markovnikoff (*Ber.*, 1897, **30**, 1211—1214). —Claim of priority in favour of Kijner (*Journ. Russ. Chem. Ges.*, 1894,

375) respecting the recognition of "hexahydrobenzene" as methylpentamethylene (Zelinsky, this vol., i, 237). A. H.

Action of Hydriodic Acid on some Cyclic Compounds at a High Temperature. By WLADIMIR B. MARKOVNIKOFF (*Ber.*, 1897, 30, 1214—1221).—[In conjunction with H. KARPOWITSCH].—When toluene is heated with hydriodic acid, the composition of the product depends on the amount of hydriodic acid employed, the temperature, and the duration of the heating. The chief product is methylhexamethylene, smaller quantities of dimethylpentamethylene and methylpentamethylene being also formed. Heptanaphthene chloride gives the same products.

[With RETZOFF and KRASCHENINNIKOFF.]—The xylenes when heated with hydriodic acid all yield toluene, whilst meta- and para-xylene in addition give a small amount of benzene. After removing the aromatic hydrocarbons, a mixture is left which consists of methylhexamethylene and methylated pentamethylenes. From the product obtained from ortho- and meta-xylene, a hydrocarbon was isolated which boils at 118—120°, has a sp. gr. = 0·7763 at 0°/0° and 0·7606 at 20°/3°. When treated with bromine, it yields tetrabromoparaxylene. No difference could be observed between the hydrocarbons yielded by the two isomerides.

When monochlorodimethylhexamethylene is heated with hydriodic acid, it yields, not only the corresponding hydrocarbon, but also products of lower boiling point, showing that decomposition has taken place.

β-Methyliodopentamethylene appears to undergo simple reduction with hydriodic acid, but the isomeric tertiary amine, $C_5H_8{:}CMe{\cdot}NH_2$, yields open chain compounds. Dimethyliodopentamethylene also yields compounds of low boiling point.

All these instances, as well as many others adduced by the author from the researches of other chemists, show that reduction with hydriodic acid at a high temperature may readily give rise to decomposition and isomerisation. Complicated side chains appear to be more readily split off than methyl, and the polymethylated cyclic compounds seem to be more easily decomposed in proportion to the number of methyl groups which they contain. A. H.

Methylcyclopentanes of Different Origin and some of their Derivatives. By WLADIMIR B. MARKOVNIKOFF (*Ber.*, 1897, 30, 1222—1226. Compare the foregoing abstracts).—Methylpentamethylene was prepared by the reduction of the iodide by the zinc copper couple, by heating amido-β-methylpentamethylene with hydriodic acid, and from β-methyladipic acid. On distillation with soda lime, this acid yields a *ketone* which boils at 143·5° (pressure = 738·5 mm.) and has a sp. gr. = 0·9314 at 0°/0°. The corresponding *alcohol* boils at 150·5—151° and yields methylpentamethylene when heated with hydriodic acid. The hydrocarbons obtained in these three ways appear to be identical. Methylpentamethylene boils at 71—72°, has a sp. gr. = 0·7662 at 0°/0° and smells like light petroleum. Bromine in presence of aluminium bromide converts it into an unstable crystalline compound melting at 120—121°.

[With MICHAIL I. KONOWALOFF and MILLER.]—The amido-compound

derived from the hydrocarbon C_6H_{12} obtained from Caucasian naphtha (Abstr., 1895, i, 454), on reduction with hydriodic acid, yields a hydrocarbon boiling at 68—73°, which probably contains some hexane. A secondary nitro-compound which was also obtained yields an *amine* which boils at 120—122° and has a sp. gr. = 0·8179 at 0°/0°. The *hydrochloride* is an amorphous mass, the *platinochloride* forms dark yellow, microscopic crystals, and the *aurochloride* crystallises in lustrous, slender plates. The amide of Aschan's acid, $C_6H_{11}\cdot COOH$, yields the same secondary amine, and the acid is therefore a methylpentamethylenecarboxylic acid. Its exact constitution has not yet been determined.

Methylpentamethylene from hexamethylene.—Amidocyclohexane and chlorocyclohexane readily yield methylpentamethylene when heated with hydriodic acid. The amido-compound is not decomposed by fuming hydrochloric acid at 250°, and the chloro-derivative can be heated by itself at 250—270° without undergoing change in this direction. The isomeric change produced by the hydriodic acid is therefore not simply due to the high temperature. A. H.

Removal of Thiophen from Benzene by means of Aluminium Chloride. By FRIEDRICH HEUSLER (*Zeit. angw. Chem.*, 1896, 750).—Benzene containing thiophen is heated for 9 hours in a reflux apparatus with about 5 per cent. of aluminium chloride, and then distilled without previous decantation. After washing the product with caustic soda and drying over calcium chloride, it is found to be free from thiophen.

In a previous communication (*Zeit. angw. Chem.*, 1896, 318), the author suggested that the benzene, after treatment with aluminium chloride, should be decanted and then distilled with steam. If this is done, however, traces of thiophen are always present, which is explained by supposing that an intermediate product is formed, somewhat soluble in benzene, and decomposed by water with regeneration of thiophen, but at the lower temperature it is only partially converted into a resin containing sulphur.

In the case of xylene, the temperature at which action takes place is higher, and consequently the intermediate product formed by the action of aluminium chloride on thioxen is quantitatively decomposed, so that the decanted xylene can be distilled with water without regeneration of thioxen. A. W. C.

Mass Law Studies. I. [Solubility of Benzene in Aqueous Alcohol.] By S. F. TAYLOR (*J. Physical Chem.*, 1897, 1, 301—303).—Varying quantities of benzene are dissolved in a given constant volume of alcohol and water added until precipitation of benzene just begins. Calling x the volume of water added and y the volume of benzene, the numbers obtained may be represented by the formula $x^{1\cdot 85}y = c$. The exponent is independent of the temperature between 20° and 35°, whilst c varies with the temperature, remaining constant, however, so long as the temperature does not change. T. E.

Sulphur and Toluene. By J. K. HAYWOOD (*J. Physical Chem.*, 1897, 1, 232—233).—A mixture of sulphur and toluene, in quantities such that two liquid layers are formed, boils at 112·05°; the toluene

employed boiled at 110°. With xylene boiling at 138·95°, in place of the toluene, the mixture boils at 143°. T. E.

Action of Sodium on Dibromomesitylene. By PAUL JANNASCH and W. HEUBACH (*Ber.*, 1897, **30**, 1073—1074).—By the action of sodium on dibromomesitylene in xylene solution, a new hydrocarbon is produced, which boils at 283—285° and melts at 103—104°; on bromination, it yields a *bromo*-derivative forming thin, broad needles melting at 235°, and on nitration, a *nitro*-compound crystallising from acetone in large, monoclinic prisms melting at 264—265°. The hydrocarbon is characterised by a remarkable tendency to crystallise from almost any solvent. J. F. T.

Action of Mercaptides on Quinones. By HARRY S. GRINDLEY and J. L. SAMMIS (*Amer. Chem. J.*, 1897, **19**, 290—295).—When dichlorodiphenoxyquinone (1 mol.) is treated in ethereal solution with sodium ethylmercaptide (6 mols.), a yellow, crystalline substance is obtained, which, when treated with water, dissolves, giving a clear solution; after a time, the aqueous solution undergoes decomposition, a green, crystalline substance separating, which is shown, on analysis, to be *tetrathioethylquinone*, $C_6O_2(SEt)_4$. This substance crystallises from alcohol in beautiful, glossy, dark green needles melting at 90—91°, and is soluble in concentrated nitric acid with evolution of oxides of nitrogen, imparting a beautiful red coloration to the acid, and is not reprecipitated on the addition of water.

On treatment with glacial acetic acid and zinc dust, it is reduced to *tetrathioethylquinol*, which crystallises from alcohol in large, colourless prisms melting at 58—59°. It is not acted on by concentrated hydrochloric acid, but dissolves in concentrated nitric or sulphuric acid, imparting to the former a bright red, and to the latter a light green colour.

Tetrathioethylquinonedibenzoyldithiobenzoylacetal,

$$C_6(SEt)_4(O{\cdot}COPh)_2(S{\cdot}COPh)_2,$$

is prepared by treating the yellow, crystalline substance, obtained by the action of sodium mercaptide on tetrathioethylquinone, with benzoic chloride. It crystallises from alcohol in two distinct forms, which are easily changed one into the other. When the solution is concentrated and cooled quickly, long, slender prisms are produced, but if the solution is dilute and allowed to cool slowly, rhombic plates are obtained. Both forms melt at 131—132°. A. W. C.

Anethoil. By EDOUARD GRIMAUX (*Bull. Soc. Chim.*, 1897, [iii], **15**, 778—779).—Anethoil, $C_6H_4Pr{\cdot}OMe$, like other ethers, is known to absorb a large quantity of hydrogen chloride. The author has studied this reaction, but has been unable to isolate any compound. The paper also contains a note on the polymerisation of anethoil. M. W. T.

Anethoil and Two of its Homologues. By CHARLES MOUREU and A. CHAUVET (*Compt. rend.*, 1897, **124**, 404—406).—Instead of distilling methylparapropiocoumaric acid as described by Perkin (this Journal, 1877, i, 411), the authors find that anethoil can be readily prepared by heating a mixture of anisaldehyde, propionic anhydride, and fused sodium propionate in equal proportions at 200°, and that it is not

necessary to first isolate the above acid. When the disengagement of carbonic anhydride has ceased, the anethoil is distilled with steam, and, after purification, first with a dilute solution of caustic soda and then with sodium bisulphite, is fractionally distilled. In a similar manner, *parabutenylanisoil*, $OMe\cdot C_6H_4\cdot CH:CHEt$, can be prepared by heating a mixture of anisaldehyde, butyric anhydride, and dry sodium butyrate, and is identical with the compound obtained by Perkin by the action of sodium carbonate on the additive product of methylparabutyrocoumaric acid and hydrogen iodide. The methylparabutyrocoumaric acid prepared by the authors melts at 129·5—131° (uncorr.), the melting point given by Perkin being 123°. *Paraisopentenylanisol*, $OMe\cdot C_6H_4\cdot CH:CHPr^{\beta}$, is obtained by heating a mixture of anisaldehyde, isovaleric anhydride, and fused sodium valerate. It has an odour of the oil of anise, boils at 248—251° (uncorr.), and has a sp. gr. = 0·977 at 0°/0°. It does not solidify even when cooled to −23°, and unites with bromine in carbon bisulphide solution. In this preparation, only traces of the unsaturated acid which is first formed could be detected amongst the products of the action. It is suggested that the characteristic odour of anethoil and of its homologues is dependent on the para-relation of the methoxy-group to the hydrocarbon chain in the molecule, and to the particular structure of this unsaturated chain.

A. C. C.

Two Modifications of Nitroso-orcinol. [Oximido-orcinol]. By FR. HENRICH (*Monatsh.*, 1897, **18**, 142—188).—This paper contains a full account of an investigation, many results of which have been described already (Abstr., 1896, i, 476). The two modifications in question have the same molecular weight, as determined in acetone solution by the ebullioscopic method, and the author inclines to the opinion that they are tautomeric, and represent respectively the enolic form,

$$CO<\begin{matrix}CH=CMe\\CH:C(OH)\end{matrix}>C:NOH,$$

and the ketonic form, $CO<\begin{matrix}CH:CMe\\CH_2-CO\end{matrix}>C:NOH$. The red ($\beta$) variety is the more soluble in most solvents; 100 c.c. of ether at 22° dissolves 1·251 gram of it, but only 0·294 gram of the yellow (α) variety. Both varieties are decidedly acid, dissolving in aqueous solutions of alkali carbonates with effervescence; they can be titrated with aqueous sodium hydroxide, phenolphthalein indicating neutrality when the monosodium salt has been formed; the dissociation constant (k) of the α-variety was found to vary from 0·0330 to 0·0210 in solutions containing 1 mol. in 457 to 3656 litres. The *potassium*, *sodium*, and *silver* salts were analysed; these must contain the metal in place of the hydrogen of the NOH group, as the silver salt, when treated with methylic iodide in cooled ethereal solution, yields a yellowish *methyloximido-orcinol*, $CO<\begin{matrix}CH=CMe\\CH:C(OH)\end{matrix}>C:NOMe$ (melting at 117°), which loses its methoxy-group when reduced, forming amido-orcinol. A dipotassium salt could not be isolated; probably, however, it is formed to some extent in solution, for a solution of the monopotassium salt (1 mol.) and potassium hydroxide (1 mol.) has a much smaller electrical con-

ductivity than corresponds with a simple mixture of the two substances. The further action of amylic nitrite in the presence of potassium hydroxide yields the green potassium salt of dioximido-orcinol,

$$CO<\genfrac{}{}{0pt}{}{CH=\!=CMe}{C(NOH)\cdot CO}>C:NOH,$$

which, as is already known, is the direct product of the action of even 1 mol. only of nitrous acid on orcinol (1 mol.) in acid solution, and which is oxidised by nitric acid to dinitro-orcinol. Treatment with benzoic chloride in the presence of aqueous soda converts oximido-orcinol into a yellowish *dibenzoyl* derivative,

$$CO<\genfrac{}{}{0pt}{}{CH=CMe}{CH:C(OBz)}>C:NOBz,$$

melting at 157—158°. Treatment with acetic anhydride and a drop of sulphuric acid in the cold converts it into a *diacetyl* derivative melting at 119—120° (wrongly described in Abstr., 1896, i, 476, as a *mon*-acetyl compound); a yellow, unstable *monacetyl* derivative, melting and decomposing at 76—77°, is formed when the potassium salt of oximido-orcinol is treated in the cold with acetic chloride in ethereal solution. By boiling orcinol in methyl-alcoholic solution with methylic iodide and sodium methoxide, and fractionating the product, *methyl-orcinol*, $OH\cdot C_6H_4Me\cdot OMe$ [1 : 3 : 5], is obtained; this boils at 144—146° under 18 mm., at 261° under 734 mm. pressure; it is converted by nitrous acid in acid solution, or by amylic nitrite in potassium hydroxide solution, into a yellowish *oximidomethylorcinol*,

$$CO<\genfrac{}{}{0pt}{}{CH=CMe}{CH:C(OMe)}>NOH,$$

melting at 119—120°, and isomeric with the compound described above. This substance can also be obtained by boiling oximido-orcinol with methylic alcohol and a little hydrochloric acid; when reduced with stannous chloride, it yields a very unstable *amidomethylorcinol*, the *hydrochloride* of which, $C_8H_9O_2\cdot NH_2,HCl$, was analysed; and, with methylic iodide and sodium methoxide, it yields yellow *dimethyloximido-orcinol*, $CO<\genfrac{}{}{0pt}{}{CH=CMe}{CH:C(OMe)}>C:NOMe$, which melts at 118°, loses one methoxy-group when reduced, forming the amidomethylorcinol just mentioned, and, when nitrated, yields yellow *dinitromethylorcinol*,

$$OH\cdot C<\genfrac{}{}{0pt}{}{CH=\!=\!=CMe}{C(NO_2)\cdot C(OMe)}>C\cdot NO_2,$$

melting and decomposing at 142—143°. C. F. B.

Condensation of Methylfurfuraldehyde with Phloroglucinol. By EMIL VOTOČEK (*Ber.*, 1897, **30**, 1195—1200).—Welbel and Zeisel have shown that, under the influence of a 12 per cent. solution of hydrochloric acid, furfuraldehyde and phloroglucinol condense in the cold (Abstr., 1895, ii, 426); and the author has now studied the action of phloroglucinol on methylfurfuraldehyde, obtained by distilling rhamnose with 12 per cent. hydrochloric acid.

Methylfurfuraldehyde phloroglucide is bright red when freshly prepared, and when washed with water, and dried in air, becomes yellow; concentrated hydrochloric acid, however, renders it reddish-brown. Analysis shows it to arise either from elimination of $2H_2O$ from 4

mols. of methylfurfuraldehyde and 3 mols. of phloroglucinol, or by elimination of $3H_2O$ from 7 mols. of methylfurfuraldehyde and 6 mols. of phloroglucinol; the substance, however, does not crystallise or melt definitely. The *benzoyl* derivative is greyish-yellow. M. O. F.

Metanitrobenzyl Derivatives. By EDUARD LUTTER (*Ber.*, 1897, **30**, 1065—1072).—The following derivatives are described. *Metamidobenzylic alcohol,* which is prepared from the corresponding nitro-compound by reduction with zinc and hydrochloric acid, forms long, glistening plates melting at 97°; the *monacetyl* derivative crystallises from benzene in needles melting at 106—107°, and the *diacetyl* derivative from a mixture of benzene and light petroleum in small, white needles melting at 67°; the *platinochloride* of the *monacetyl base* forms long, thin needles darkening at 196°.

Metanitrobenzylic thiocyanate, $NO_2\cdot C_6H_4\cdot CH_2\cdot SCN$ [$NO_2 : CH_2\cdot S\cdot CN = 1 : 3$], formed when metanitrobenzylic chloride is mixed with potassium thiocyanate in alcoholic solution, forms pale yellow, glistening needles melting at 75—76° after recrystallisation from hot alcohol. On treatment with concentrated sulphuric acid, it yields *metanitrobenzylic thiocarbamate,* $NO_2\cdot C_6H_4\cdot CH_2\cdot S\cdot CO\cdot NH_2$, which separates from amylic alcohol in small crystals melting at 121·5°; on boiling with a 20 per cent. solution of hydrochloric acid for 2 hours, this is converted into *metanitrobenzylic mercaptan,* $NO_2\cdot C_6H_4\cdot CH_2\cdot SH$, crystallising in yellowish-white needles melting at 11—12°; on oxidation with iodine, this mercaptan gives *metanitrobenzylic bisulphide,* $(NO_2\cdot C_6H_4\cdot CH_2)_2S_2$, which crystallises from alcohol in microscopic needles melting at 103—104°; and on reduction with stannous chloride yields the hydrochloride of *metamidobenzylic mercaptan,* $NH_2\cdot C_6H_4\cdot CH_2\cdot SH,HCl$, which is deposited from concentrated hydrogen chloride in small crystals melting and decomposing at 167°; the hydrochloride of *metamidobenzylic bisulphide* crystallises in small, white scales, which, however, do not melt.

Metanitrobenzylic methylic sulphide, $NO_2\cdot C_6H_4\cdot CH_2\cdot SMe$, formed when methylic alcohol reacts with metanitrobenzylic mercaptan in the presence of sodium methoxide, crystallises in long, white needles melting at 31°, and on reduction passes into the hydrochloride of *metamidobenzylic methylic sulphide,* $SMe\cdot C_6H_4\cdot NH_2,HCl$; this crystallises in colourless needles readily soluble in alcohol and amylic alcohol; the *base* is a nearly colourless oil.

Metanitrobenzylic sulphide, $(NO_2\cdot C_6H_4\cdot CH_2)_2S$, formed when a methyl alcoholic solution of metanitrobenzylic mercaptan reacts with a methyl alcoholic solution of metanitrobenzylic chloride in the presence of sodium methoxide, crystallises from alcohol in glistening leaflets melting at 109—110°. J. F. T.

Cholesterol. By CH. CLOËZ (*Compt. rend.*, 1897, **124**, 864—866). —When a solution of bromine in carbon bisulphide is gradually added to a solution of cholesterol in the same solvent, both being cooled to − 15°, the liquid suddenly becomes filled with minute, acicular crystals which redissolve as the addition of bromine is continued, the cholesterol being converted into the dibromide $C_{26}H_{44}OBr_2$. The crystalline precipitate is readily isolated, and has the empirical composition

$C_{26}H_{44}OBr$, but it is really a molecular compound of cholesterol and its dibromide, $C_{26}H_{44}OBr_2,C_{26}H_{44}O$, and can be formed by mixing, at $-15°$, molecular proportions of its proximate constituents dissolved in carbon bisulphide. It melts and decomposes at 112°, is very soluble in chloroform, ether, and benzene, and also in carbon bisulphide except at low temperatures. It is only slightly soluble in alcohol at the ordinary temperature, but dissolves readily at 70°, and this fact can be utilised for purifying the compound. Attempts to separate the compound into its components by the action of various solvents gave negative results; it either remained unaltered, or was converted into resinous products, especially if heated. C. H. B.

Carbamide Derivatives of Orthoamidobenzylamine. By CARL PAAL and BR. HILDENBRAND (*J. pr. Chem.*, 1897, [ii], **55**, 238—248).—Diphenylorthoamidobenzylcarbamide,

$$NH_2\cdot C_6H_4\cdot CH_2\cdot NPh\cdot CO\cdot NHPh$$

(Abstr., 1891, 944; 1894, i, 186), can be obtained by reducing the nitro-compound either with tin and hydrochloric acid in alcoholic solution or with zinc and acetic acid. The yellow *platinochloride*, $(C_{20}H_{19}N_3O)_2,H_2PtCl_6$, melts at 187°; the *stannochloride* decomposes at 172°, and is partially decomposed by water; the yellow *picrate*, $C_{20}H_{19}N_3O,C_6H_3N_3O_7$, melts at 164°. With acetic anhydride at the ordinary temperature, it yields an *acetyl* derivative, melting at 145°, and when warmed with benzoic acid for a few minutes, a *benzoyl* derivative melting at 170°. When warmed with phenylic cyanate in benzene solution, it is converted almost quantitatively into *orthophenylureidobenzyldiphenylcarbamide*, $NHPh\cdot CO\cdot NH\cdot C_6H_4\cdot CH_2\cdot NPh\cdot CO\cdot NHPh$, which melts at 139—140°, and when heated above its melting point, decomposes into diphenylcarbamide and *3'-phenyl-2'-ketotetrahydroquinazoline*, $C_6H_4<\begin{matrix}NH\cdot CO\\ |\quad\;\; |\\ CH_2\cdot NPh\end{matrix}>$, which melts at 186—188°. With phenylic thiocyanate, an analagous *thio*-compound, melting at 222°, is formed, but this yields no quinazoline when heated.

Phenylorthoamidobenzylparatolylcarbamide,

$$NH_2\cdot C_6H_4\cdot CH_2\cdot N(C_6H_4Me)\cdot CO\cdot NHPh$$

(Abstr., 1894, i, 187), yields a similar series of compounds, of which the names and melting points are here given. *Stannochloride*, 174°; *hydrochloride*, $C_{21}H_{21}N_3O,HCl$, 156°; *platinochloride*,

$$(C_{21}H_{21}N_3O)_2,H_2PtCl_6,$$

yellow, 183°; *oxalate*, $C_{21}H_{21}N_3O,C_2H_2O_4 + 3\frac{1}{2}H_2O$, 166° (when anhydrous); *picrate*, $C_{21}H_{21}N_3O,C_6H_3N_3O_7$, yellow, 156°. *Acetyl*, 141°, and *benzoyl*, 192—193°, derivatives. *Ureido*-compound, 135°; *3'-paratolyl-2'-ketotetrahydroquinazoline*, 218°. *Thioureido*-compound, 230—231°.

C. F. B.

Halogenated Diazonium Chlorides. By BENNO HIRSCH (*Ber.*, 1897, **30**, 1148—1153).—Pure, neutral, halogenated diazonium chlorides are only obtained from the hydrochlorides of chlor-, brom-, or iod-aniline, on treatment with amylic nitrite, when the former are absolutely free from the last traces of free acid, so that in the preparation of the following compounds it was found necessary to prepare the hydrochlorides by passing dry hydrogen chloride into a solution of the

amine in absolute alcohol, and then to heat the product at 30—40°, until the last traces of acid had been removed. *Parabromodiazonium chloride* consists of fine, white crystals, which are somewhat hygroscopic, the *pariodo*-compound forming white needles, very insoluble in absolute alcohol. *Orthochlorodiazonium chloride*, and *metachlorodiazonium chloride* are white, crystalline, neutral salts; nitrogen is slowly eliminated from the ortho- and meta-compounds in alcoholic solutions, but the *para*-derivative is stable. J. F. T.

Acid Diazonium Chlorides. By ARTHUR R. HANTZSCH (*Ber.*, 1897, **30**, 1153—1158).—There are two types of acid diazonium chlorides, namely the mon-acid salt, $R\cdot N_2Cl,HCl$, and the tri-acid salt, $3RN_2Cl,HCl$, *tri-acid parabromodiazonium chloride*, $3C_6H_4Br\cdot N_2Cl,HCl$, formed when the diazotisation is carried out in presence of excess of hydrochloric acid, crystallises in needles. The *tri-acid trichlorodiazonium chloride*, $3C_6H_2Cl_3\cdot N_2Cl,HCl$, is formed in the same way.

Monacid tribromobenzenediazonium chloride, $C_6H_2Br_3\cdot N_2Cl,HCl + 4H_2O$, forms white, microscopic crystals readily soluble in water, and shows all the reaction of a diazonium salt. J. F. T.

Two Isomeric Triethylidenediphenylhydrazines. By HENRI E. CAUSSE (*Compt. rend.*, 1897, **124**, 197—200).—*α-Triethylidenediphenylhydrazine*, $C_{18}H_{22}N_4$, is formed when a solution of acetaldehyde in aqueous phosphoric acid (24·6 grams H_3PO_4 per litre) is added to a solution of sodium thiosulphate (25 grams) in water (500 c.c.) containing 20 grams of phenylhydrazine. The crystals which separate are washed with water, dried, treated with alcohol, and filtered in order to remove the insoluble isomeride. The alcoholic solution on evaporation leaves a crystalline mass of the α-compound, which, when washed with ether and dried in an atmosphere of carbonic anhydride, melts at 60°. When exposed to the air, it increases in weight and becomes yellow. It is but slightly soluble in cold water, dissolves in alcohol and ether; less readily in benzene and light petroleum. From hot water, it separates in colourless, leaf-like crystals. It does not reduce Fehling's solution, and is not acted on by caustic alkalis; but reduces solutions of mercuric chloride and silver nitrate. With acid chlorides, it reacts with difficulty, substitution products of phenylhydrazine being formed. On mixing alcoholic solutions of this compound and of benzaldehyde, *dibenzylidenediphenylhydrazine*, $C_{26}H_{24}N_4 + \frac{1}{2}H_2O$, separates out after some days in long needles melting at 156°. *β-Triethylidenediphenylhydrazine* is prepared by adding a mixture of acetaldehyde (25 grams), normal aqueous phosphoric acid (50 grams), and water (175 grams) gradually to a mixture of normal phosphoric acid (825 grams), glycerol (150 grams), and phenylhydrazine (20 grams). A granular precipitate consisting of both isomerides is formed, from which the β-compound can be obtained by washing first with water, and then with alcohol. From boiling alcohol, it separates in colourless prisms melting at 99·5°, which are stable in the air, very slightly soluble in hot, insoluble in cold water, and but slightly soluble in alcohol, benzene, and ether in the cold. It is very stable, being practically unacted on by acids, alkalis, acid chlorides, and benz-

aldehyde, and does not reduce Fehling's solution. The author is of opinion that these two isomerides have the following formulæ:

$$(\alpha)\ CHMe(NPh{\cdot}N{:}CHMe)_2. \quad (\beta)\ N\begin{matrix}\diagup\text{———CHMe———}\diagdown \\ \text{—NPh·CHMe·NPh—} \\ \diagdown\text{———CHMe———}\diagup\end{matrix}N.$$

A. C. C.

Unsymmetrical Phenylhydrazine Derivatives. By Hans Rupe and Joh. Všetečka (*Ber.*, 1897, **30**, 1101. Compare Abstr., 1895, i, 521; 1896, i, 429).—Chloracetodimethylparaphenylenediamine (m. p. 146—147°) obtained by the action of chloracetic chloride on dimethylparaphenylenediamine, reacts with phenylhydrazine, yielding *phenylhydrazido-acetodimethylparaphenylenediamine*,

$$NH_2{\cdot}NPh{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}NMe_2,$$

which crystallises in yellowish needles, and melts at 134—135°. The compounds with benzaldehyde, ethylic acetoacetate, and acetic chloride melt respectively at 184—185°, 185°, and 158°. Its nitroso-derivative, $NO{\cdot}NPh{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}NMe_2$, melting at 165°, is identical with that obtained from anilidoacetodimethylparaphenylenediamine (m. p. 132—134°).

J. J. S.

The Ketonehydrazones of Aromatic Hydrazines. By August Arnold (*Ber.*, 1897, **30**, 1015—1017).—Acetonephenylhydrazone reacts vigorously with phenylcarbimide to form a compound which melts at 196°, and is very sparingly soluble in the ordinary solvents. The same substance appears to be formed in a similar way from the phenylhydrazone of methyl ethyl ketone, and from ethylidenephenylhydrazone, but its constitution has not yet been ascertained. Acetone phenylhydrazone readily combines with isocyanic acid to form *acetonephenylhydrazonesemicarbazide*, $NH_2{\cdot}CO{\cdot}NPh{\cdot}N{:}CMe_2$, which crystallises in white needles melting at 140°. When boiled with water, it yields acetone and phenylhydrazinesemicarbazide.

Methylethylketonephenylhydrazone-thiosemicarbazide,

$$NHPh{\cdot}CS{\cdot}NPh{\cdot}N{:}CMeEt,$$

crystallises in slender needles melting at 174°. The corresponding *semicarbazide* forms slender plates melting at 168°.

Acetoneparatolylhydrazone hydrochloride crystallises in slender needles melting at 135°, whilst the *hydrobromide* melts at 195°; the *nitrate* is also a crystalline substance. The *phenylthiosemicarbazide*,

$$NHPh{\cdot}CS{\cdot}N(C_6H_4Me)N{:}CMe_2,$$

forms white needles melting at 164°.

A. H.

Phenylnitromethane [exo-Nitrotoluene]. By Arnold F. Holleman (*Rec. trav. Chim.*, 1896, **15**, 356—364, 365—369. Compare Abstr., 1895, i, 455, and 1896, i, 148).—Benzoic chloride reacts with a methylic alcoholic solution of sodium phenylnitromethane, yielding dibenzhydroxamic acid, the melting point of which the author gives as 161°, and not 153°. Paranitrobenzoic chloride reacts with sodium phenylnitromethane suspended in dry benzene, yielding a mixture of *dinitrodibenzoylbenzhydroxamic acid*,

$$NO_2{\cdot}C_6H_4{\cdot}CO{\cdot}O{\cdot}CPh{:}NO{\cdot}CO{\cdot}C_6H_4{\cdot}NO_2,$$

and *nitrobenzoylhydroxamic acid*, $OH{\cdot}CPh{:}NO{\cdot}CO{\cdot}C_6H_4{\cdot}NO_2$. These

two compounds are readily separated by N/10 sodium hydroxide, which dissolves the mononitro-derivative melting at 168°, and leaves the dinitro-derivative; the latter, after crystallisation from benzene, melts at 187°; it is probably contaminated with a small quantity of paranitrobenzoic anhydride, which melts at 186°. The dinitro-derivative, when heated in a sealed tube with concentrated hydrochloric acid, decomposes, yielding benzoic and paranitrobenzoic acids.

Benzoylnitrobenzhydroxamic acid, $NO_2 \cdot C_6H_4 \cdot C(OH)\colon NOBz$, obtained by the action of benzoic chloride on potassium paranitrophenylnitromethane, crystallises from its acetic acid solution in colourless plates, and melts and decomposes at 187°. When heated with concentrated hydrochloric acid at 150—160° for 3 hours, it is completely decomposed into hydroxylamine, benzoic acid, and paranitrobenzoic acid. It is readily soluble in alkalis, and is precipitated unaltered on the addition of acids, but if the precipitate is left in contact with the acid liquid for several hours, it is gradually transformed into an isomeric compound sparingly soluble in alkalis.

Paranitrophenylnitromethane [*ω*:4-*dinitrotoluene*] $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot NO_2$, obtained by the action of paranitrobenzylic iodide on silver nitrite, crystallises in glistening plates, and melts at 90°. The *potassium* derivative, $NO_2 \cdot C_6H_4 \cdot CHK \cdot NO_2 + 2H_2O$, is very characteristic, crystallising in small, glistening, red crystals. *Orthonitrophenylnitromethane* [*ω*:2-*dinitrotoluene*], obtained in a similar manner, melts at 72°, and also yields a potassium derivative with $1H_2O$, crystallising in glistening, red needles. J. J. S.

Action of Sodium Ethoxide on Bromamides. By S. E. SWARTZ (*Amer. Chem. J.*, 1897, **19**, 295—319).—Sodium ethoxide in alcoholic solution acts on amides and bromamides in two ways; firstly, as a reducing agent, thereby regenerating the acid amide, and secondly as a rearranging agent, changing the amidobromide to a bromoformamide or carbimide. The latter may react with the alcohol present, forming a urethane, or with the acid amide, generated by the reduction of the bromamide forming a substituted carbamide; or it may be hydrolysed, thus producing an amine. The products of the change depend on the concentration of the solution and on the nature of the bromamide used. In concentrated solution, the acid amide is regenerated, whilst in more dilute solutions, rearrangement, with the formation of urethanes or ureas, takes place; and in very dilute solutions hydrolysis of the carbimide occurs, with the production of an amine.

When sodium methoxide acts on succinimide bromide in benzene solution, 70 per cent of the theoretical amount of succinimide and a considerable amount of tar are produced, but no urethane or substituted hydroxylamine. If sodium ethoxide is used, varying amounts of succinimide and diethylic succino-β-ureidopropionate melting at 78° are formed.

When benzamide bromide is slowly added to a well-cooled solution of sodium ethoxide in absolute alcohol, reaction takes place slowly, as indicated by a gradual rise in temperature; the solution becomes brownish-red, and on cooling benzoylphenylcarbamide separates, whilst the alcoholic mother liquor contains phenylurethane and benzamide.

The action of sodium ethoxide on the isomeric nitrobenzamide bromides has also been studied. The para-compound yields paranitrophenylurethane, paranitrobenzoylparanitrophenylcarbamide, and paranitrobenzamide; and the ortho- and meta-compounds, the corresponding ortho- and meta-urethanes, carbamides, and amides.

The author has examined the action of phosphorus pentachloride on the nitrophenylurethanes produced in the above experiments in order to ascertain if the production of chloro-formamides and carbimides by the reaction is a general one, and also for the closer investigation of the properties of such substances.

When phosphorus pentachloride and methylorthonitrophenylurethane are mixed in molecular proportion and gently warmed, reaction takes place, and methylic chloride is disengaged. The slightly yellowish liquid product, when cooled in a freezing mixture, deposits needle-shaped crystals melting at 47°, which prove to be chloro-formorthonitranilide.

If, instead of isolating the chloroformorthonitranilide as above, the phosphorus oxychloride is distilled off in a current of dry hydrogen chloride, and the residue heated in a current of dry air until no more hydrogen chloride is given off, orthonitrophenylcarbimide is formed, which may be extracted with light petroleum. It crystallises readily in clusters of delicate, needle-shaped crystals, and melts at 41°. With water, it yields nitraniline, and with ethylic and methylic alcohols it gives the corresponding urethanes. When left for some time in a vacuum, it is changed into a crystalline substance melting at 220°, which is probably a cyanurate. The same substance is produced when chloroformorthonitranilide is allowed to remain for some time.

Isopropylic orthonitrophenylcarbamate, $NO_2 \cdot C_6H_4 \cdot NH \cdot COOPr^{\beta}$, is formed by the interaction of isopropylic alcohol and orthonitrophenylcarbimide; it crystallises from light petroleum in yellow cubes, which melt at 12°. The corresponding *isobutyl* derivative forms yellow crystals melting at 13°, the *normal amyl* derivative crystals melting at $-5°$.

Glycol nitrophenylmonocarbamate, $NO_2 \cdot C_6H_4 \cdot NH \cdot COO \cdot C_2H_4 \cdot OH$, a yellow, crystalline substance melting at 71° without decomposition, is formed by the action of glycol on the above-mentioned carbimide; it is not affected by cold alkalis or dilute acids, but, on heating, they readily decompose it. By varying the proportions of glycol and carbimide, the glycol dicarbamate can be obtained as a yellow, crystalline substance melting at 160°.

Orthonitrocarbanilide, $NO_2 \cdot C_6H_4 \cdot NH \cdot CO \cdot NHPh$, is obtained as an almost white, crystalline substance melting at 170°, when the carbimide is treated with the molecular quantity of aniline in ethereal solution.

Orthonitrophenylcarbamide, $NO_2 \cdot C_6H_4 \cdot NH \cdot CO \cdot NH_2$, is formed when an ethereal solution of orthonitrophenylcarbimide is saturated with dry gaseous ammonia; the crystals melt at 181°.

Symmetrical orthonitrophenylorthotolylurea,

$$NO_2 \cdot C_6H_4 \cdot NH \cdot CO \cdot NH \cdot C_6H_4Me,$$

is obtained as a crystalline substance melting at 189° when orthotolui-

dine acts on orthonitrophenylcarbimide in ethereal solution. It closely resembles orthonitrocarbanilide in all its properties.

Orthonitrophenyldimethylcarbamide, $NMe_2 \cdot CO \cdot NH \cdot C_6H_4 \cdot NO_2$, is formed when dry methylamine is passed into an ethereal solution of orthonitrophenylcarbimide, warmed until a test with aniline gives no precipitate of orthonitrocarbanilide; it is an oil which does not solidify at $-30°$. The corresponding *diethyl*, *dipropyl*, *dibutyl*, and *diamyl* compounds are all oils, formed by methods precisely similar to the above.

Chloroformoparanitranilide, prepared in the same manner as the corresponding ortho-compound, is a white substance with a very penetrating odour. When heated, it loses hydrogen chloride, and at 75° is converted into the carbimide.

Paranitrophenylcarbimide, prepared as above, crystallises from light petroleum in concentric clusters of white needles which melt at 44°. Water decomposes it, giving nitraniline, and with amines and alcohols carbamides and urethanes are formed. On standing, it is polymerised, the change being hastened by heating.

Isopropylparanitrophenylurethane, formed by the interaction of isopropylic alcohol and this carbimide, melts at 78°; the corresponding isobutyl compound melts at 62°.

Paranitrocarbanilide is obtained as a precipitate melting at 209°, when aniline is added to an ethereal solution of paranitrophenylcarbimide.

A. W. C.

Hydrolysis of Acid Amides. By IRA REMSEN (*Amer. Chem. J.*, 1897, **19**, 319—321).—The relative ease with which the three nitrobenzamides are converted into their ammonium salts by dilute acids has been studied. The results obtained show that the ortho-amide resists the action of the hydrolysing agent to a marked degree, whereas the meta- and para-amides are readily affected, the para somewhat more so than the meta.

The author proposes investigating the method more fully in order to ascertain whether the influence of ortho-groups on the hydrolysis of acid amides is always the same; and how various atoms and groups differ in their effect on the rate of hydrolysis.

A. W. C.

Orthobromoparethoxyphenylsuccinimide (Bromopyrantine). By ARNALDO PIUTTI (*Ber.*, 1897, **30**, 1170—1174).—*Orthobromoparethoxyphenylsuccinimide*, $OEt \cdot C_6H_3Br \cdot N{<}\begin{matrix} CO \cdot CH_2 \\ | \\ CO \cdot CH_2 \end{matrix}$, obtained by the action of bromine on the imide in glacial acetic acid, crystallises from alcohol in colourless needles melting at 150—151°; when heated with concentrated hydrochloric acid in a reflux apparatus, it yields orthobromoparaphenetidine hydrochloride. The free base, which has been recently described by Hodurek (this vol., i, 276), crystallises in the rhombic system; $a : b : c = 0{\cdot}7425 : 1 : 0{\cdot}8433$. The *phthalyl* derivative crystallises in colourless needles melting at 195—196°; it is produced by the action of phthalic anhydride on the base, and is also formed when bromine acts on parethoxyphenylphthalimide. The *succinyl* derivative melts at 150—151°.

Orthobromoparethoxyphenylsuccinamic acid,

$$OEt{\cdot}C_6H_3Br{\cdot}NH{\cdot}CO{\cdot}C_2H_4{\cdot}COOH,$$

is produced when the imide is hydrolysed with alcoholic potash, and crystallises from alcohol in white needles melting at 149—150°; the *silver* salt is crystalline.

Orthobromoparaphenetidine hydrochloride has more pronounced toxic properties than phenacetine and pyrantine; it also acts vigorously on blood, and converts oxyhæmoglobin into methæmoglobin. Orthobromoparethoxyphenylsuccinimide, however, does not give rise to functional derangement, probably owing to its insoluble character.

M. O. F.

2 : 5-Dichlorobenzaldehyde. By ROBERT GNEHM and EMIL BÄNZIGER (*Annalen*, 1897, **296**, 62—84. Compare Abstr., 1896, i, 432).—The main facts recorded in this paper have already appeared (*loc. cit.*)

M. O. F.

Salicylaldehyde. By FRITZ BLAU (*Monatsh.*, 1897, **18**, 123—137). —The substance obtained by Möhlau (Abstr., 1886, 1033), by condensing salicylaldehyde with aniline in the presence of zinc chloride, is, as he thought, acridine, and not phenanthridine. A better yield is obtained by using ready-formed "salhydranilide" ($OH{\cdot}C_6H_4{\cdot}CH{:}NPh$), with phosphoric anhydride as a condensing agent, but even then the yield is extremely small.

When an attempt was made to use strong sulphuric acid as a condensing agent, and salhydranilide was heated with five times its weight of the acid for an hour on the water bath, *orthohydroxybenzylideneanilinesulphonic acid*, $OH{\cdot}C_6H_3(SO_3H){\cdot}CH{:}NPh$, was formed; this crystallises from water in yellow needles containing $1H_2O$; its solution in water is less yellow than those of its salts; of these, the crystalline *sodium*, $C_{13}H_{10}NSO_4Na,C_{13}H_{11}NSO_4$; *barium*, $(C_{13}H_{10}NSO_4)_2Ba + 4H_2O$, and *silver*, $C_{13}H_{10}NSO_4Ag + 2H_2O$ (or anhydrous) salts were prepared. These are much less stable than the free acid, and decompose readily in aqueous solution into aniline and salts of *salicylaldehydesulphonic acid*, $OH{\cdot}C_6H_3(SO_3H){\cdot}CHO$. This acid is best prepared by boiling salhydranilide with baryta water or with aqueous sodium carbonate; the *sodium*, $C_7H_5SO_5Na + 2H_2O$; *barium*, $(C_7H_5SO_5)_2Ba + H_2O$ and $C_7H_4SO_5Ba + 3H_2O$, and *silver*, $C_7H_5SO_5Ag$, salts were prepared and analysed. With phenylhydrazine, the acid yields the *phenylhydrazine* salt of the *phenylhydrazonesulphonic acid*, $C_{19}H_{20}N_4O_4S$, and it is oxidised by silver oxide to the acid $OH{\cdot}C_6H_3(SO_3H){\cdot}COOH$, obtained by direct sulphonation of salicylic acid; this acid yields no azo-dyes with diazochloride solutions, from which circumstance it is inferred that the para-position relative to the hydroxyl group is occupied, in which case the acid must have the composition [$COOH : OH : SO_3H = 1 : 2 : 5$]. This is the first time that a sulphonic acid of salicylaldehyde has been prepared.

C. F. B.

Some Derivatives of Salicylaldehyde. By PAUL RIVALS (*Compt. rend.*, 1897, **124**, 368—370).—The author confirms Etting's statement that the compound of salicylaldehyde and caustic potash, $C_7H_6O_2,KOH$, loses water in a vacuum at 120°, yielding the derivative

$C_7H_5O_2K$. The following numbers for the heat of formation of this compound are given :

$C_7H_6O_2$ liq. + KOH sol. = $C_7H_5O_2K,H_2O$ sol. ...... + 18·6 Cal.

$C_7H_6O_2$ liq. + KOH sol. = $C_7H_5O_2K$ sol. + H_2O sol. + 21·5 Cal.

the latter number being identical with the heat of formation of the isomeric benzoate, and much higher than that of the phenoxides. By the action of acetic chloride on salicylaldehyde, the author has obtained both acetosalicyl (melting at 35° and boiling at 253°) and parasalicyl as described by Perkin. The molecular weight of parasalicyl determined by the cryoscopic method agrees with the formula $C_{14}H_{10}O_3$. Its molecular heat of combustion is 1589·7 Cal. (const. volume) and 1590·3 Cal. (const. pressure), the deduced heat of formation of solid parasalicyl from its elements being + 74·9 Cal. Its heat of formation from the aldehyde would be :

$2C_7H_6O_2$ liq. = $C_{14}H_{10}O_3$ sol. + H_2O sol.... + 26·2 Cal.

Since all anhydrides are formed from their elements with absorption of heat, the above number is incompatible with the constitutional formula $CHO \cdot C_6H_4 \cdot O \cdot C_6H_4 \cdot COH$ assigned to parasalicyl by Perkin. The ease with which dialdehydes undergo transformation into unsymmetrical compounds with development of heat renders it probable that parasalicyl is such a compound. A. C. C.

Derivatives of Acetophenone. By Siegmund Gabriel and Georg Eschenbach (*Ber.*, 1897, **30**, 1126—1129).—A slightly acidified solution of ω-amido-acetophenone hydrochloride, when treated with sodium amalgam ($2\frac{1}{2}$ per cent.), yields acetophenone and ammonia. The oxime of ω-phenoxyacetophenone (Fritz, Abstr., 1896, i, 151), when reduced with sodium amalgam and alcohol, yields phenol and α-phenylethylamine, $NH_2 \cdot CHMePh$.

ω-Amido-acetophenoneoxime crystallises in reddish-yellow, flat needles and melts at 140°. The authors have prepared ω-cyanacetophenone by the action of an alcoholic solution of potassium cyanide on ω-bromacetophenone ; the yield is 60 per cent. of the theoretical. When the cyano-derivative is reduced with sodium amalgam, it yields the nitrile of β-phenyl-β-lactic acid, $OH \cdot CHPh \cdot CH_2 \cdot CN$, which, when further reduced with sodium and alcohol, yields phenylpropylamine. The hydroxy-nitrile combines apparently with hydrogen bromide yielding a *compound*, $C_9H_9NO + 2HBr$, which melts at 116°. Concentrated hydrochloric acid in the cold hydrolyses the hydroxy-nitrile with formation of *β-phenyl-β-lactamide*, $OH \cdot CHPh \cdot CH_2 \cdot CO \cdot NH_2$, which melts at 119—120°. The amide, when heated with hydrochloric acid (15 per cent.), yields cinnamic acid. J. J. S

Action of Alcohols on Isoimides. By P. Hojonides van der Meulen (*Rec. trav. Chim.*, 1896, **15**, 323—348. Compare this vol., i, 281).—Alcohols as a rule react with isoimides or their hydrochlorides (Abstr., 1896, i, 314), yielding the corresponding ethereal salts of the amido-acids. Methylic alcohol reacts with α-camphorisoimide hydrochloride, forming methylic α-camphoramate, $NH_2 \cdot CO \cdot C_8H_{14} \cdot COOMe$, which melts at 152—153° ; the same salt is obtained when hydrogen chloride is passed into a solution of cyanolauronic acid (Oddo and Leonardi, this vol., i, 86).

Methylic α-camphormethylamate, $NHMe\cdot CO\cdot C_8H_{14}\cdot COOMe$, melts at 135—136°. *Methylic β-camphoramate*, which may be obtained either from β-camphorisoimide hydrochloride, or by passing hydrogen chloride into a methyl alcoholic solution of β-camphoramic acid, can be crystallised from water, melts at 138—142°, and is readily hydrolysed. The corresponding *ethylic* salt melts at 94°.

Methylic β-camphormethylamate, obtained from β-camphormethylamic acid, melts at 68°; it is best isolated by the addition of light petroleum to its benzene solution.

Methylic β-hemipinamate, $C_6H_2(OMe)_2(COOMe)\cdot CONH_2$ [3 : 4 : 1 : 2], can be obtained from β-hemipinisoimide or from cyanodimethoxybenzoic acid, [OMe_2 : COOH : CN = 3 : 4 : 1 : 2] (Abstr., 1896, i, 315); it melts at 173—174°.

Ethylic β-hemipinamate melts at 180—181°, and is at the same time converted into the imide.

Methylic α-hemipinobenzylamate, $C_6H_2(OMe)_2(CO\cdot NH\cdot C_7H_7)\cdot COOMe$ [3 : 4 : 1 : 2], melts at 96—97°, and the *methylic* salt of the corresponding β-acid at 113°.

Methylic succinophenylamate, $COOMe\cdot C_2H_4\cdot CO\cdot NHPh$, was obtained from succinophenylamic acid by first converting it into its isoimide, and treating the latter with methylic alcohol; it is thrown down from its acetone solution on the addition of water, and melts at 91—96°. *Methylic succinobenzylamate*, $COOMe\cdot C_2H_4\cdot CO\cdot NH\cdot C_7H_7$, when precipitated from its benzene solution by the addition of light petroleum, melts at 61—64°. *Methylic phthalophenylamate*,

$$COOCH_3\cdot C_6H_4\cdot CO\cdot NHPh,$$

melts at 111—113·5°, and is readily soluble in most organic solvents with the exception of light petroleum.

Certain isoimide hydrochlorides react with alcohols, yielding substances isomeric with the normal ethereal salts, whilst in other cases the product consists of a mixture of the normal and iso-ethereal salt, for example, phthalophenylisoimide.

Iso-methylic α-hemipinamate hydrochloride,

$$C_6H_2(OMe)_2{<}\begin{matrix}C(NH_2)(OMe)\\ \text{——}CO\text{——}\end{matrix}{>}O,HCl,$$

melts and decomposes at about 141°, and is readily soluble in water and in alkali hydroxides or carbonates. The same compound is formed when cyanodimethoxybenzoic acid, [$(OMe)_2$: CN : COOH = 3 : 4 : 1 : 2] (Abstr., 1896, i, 315), is dissolved in methylic alcohol and the solution saturated with hydrogen chloride. It yields an *aurochloride* crystallising in yellow plates. The hydrochloride, when treated with potassium nitrite, yields α-methylic hemipinate melting at 120—122°.

Iso-methylic phthalophenylamate hydrochloride,

$$C_6H_4{<}\begin{matrix}C(NHPh)(OMe)\\ \text{——}CO\text{——}\end{matrix}{>}O,HCl,$$

obtained by the action of methylic alcohol on phthalophenylisoimide hydrochloride, is decomposed by cold water, yielding the free *isomethylic* salt, $C_6H_4{<}\begin{matrix}C(NHPh)(OMe)\\ \text{——}CO\text{——}\end{matrix}{>}O$, or $COOH\cdot C_6H_4\cdot C(OMe)\colon NPh$, which melts at 123°, and is readily soluble in alkalis or alkali carbonates. The hydrochloride is readily decomposed by boiling water, yielding

phthalophenyldiamide, which is insoluble in the usual solvents, but crystallises from nitrobenzene in small needles melting at 251—252°. The *silver* salt of the isomethylic salt is also described. J. J. S.

Amidines of the Anthranilic Acids. By M. KOWALSKI and STEFAN VON NIEMENTOWSKI (*Ber.*, 1897, **30**, 1186—1193).—*Ethenyldianthranilic acid*, $COOH\cdot C_6H_4\cdot NH\cdot CMe{:}N\cdot C_6H_4\cdot COOH$, is obtained by hydrolysing the anhydride with aqueous sodium carbonate, and crystallises in long, transparent needles melting at 226°. The *anhydride*, $C_6H_4<\begin{matrix}N\cdot CMe{:}N\cdot C_6H_4\cdot COOH\\ | \\ CO\end{matrix}$, is produced on heating acetanthranilic acid with acetic anhydride ($2\frac{1}{2}$ mols.) during 50 hours; the liquid is poured into water, and the precipitate extracted with boiling water to remove unaltered acetanthranilic acid, the residue being finally crystallised fractionally from alcohol. The anhydride separates from glacial acetic acid in white scales, softens at 240°, and melts at 248°.

The *anhydride* of ethenyldimetahomoanthranilic acid,

$$C_6H_3Me<\begin{matrix}N\cdot CMe{:}N\cdot C_6H_3Me\cdot COOH\\ | \\ CO\end{matrix},$$

is formed when metahomoanthranilic acid is treated with boiling acetic anhydride, and crystallises from alcohol in white scales melting at 293°; it is insoluble in water and ether, and dissolves very sparingly in boiling benzene; when treated with boiling alkalis, it yields metahomoanthranilic acid. The *amide* of the anhydride,

$$C_6H_3Me<\begin{matrix}N\cdot CMe{:}N\cdot C_6H_3Me\cdot CONH_2\\ | \\ CO\end{matrix},$$

is produced simultaneously with the foregoing substance, from which it may be separated by its more sparing solubility in alcohol; it crystallises in somewhat indefinite brown scales, and melts at 278°. Boiling caustic soda converts the amide into a *compound* which crystallises from alcohol in long, lustrous needles and melts at 235—240°.

Pyruvodianthranilic acid,

$$COOH\cdot C_6H_4\cdot N{:}C(COMe)\cdot NH\cdot C_6H_4\cdot COOH,$$

is prepared by heating anthranilic and pyruvic acids with toluene in a reflux apparatus; it crystallises from alcohol in small, yellowish needles, and melts at 295°. The *phenylhydrazone* softens at 165—170°, and melts and effervesces at 250°.

Pyruvodimetahomoanthranilic acid,

$$COOH\cdot C_6H_3Me\cdot N{:}C(COMe)\cdot NH\cdot C_6H_3Me\cdot COOH,$$

crystallises from water or alcohol in straw yellow needles, and melts, decomposing, at 280°. The *phenylhydrazone* forms bright yellow needles and softens at 202°; it melts and decomposes at 206°.

M. O. F.

Anthranilic Acid Derivatives. By HANS RUPE (*Ber.*, 1897, **30**, 1097—1100).—Anthranilic acid cannot be directly nitrated; acetylanthranilic acid, however, when dissolved in concentrated sulphuric acid, and then treated with a mixture of nitric (sp. gr. 1·44) and sulphuric acids, yields *metanitroacetanthranilic acid*,

$$NO_2\cdot C_6H_3(NHAc)\cdot COOH.$$

This acid crystallises from its hot, aqueous solution in yellow needles and melts at 152°. When heated with 50 per cent. sulphuric acid, or with concentrated potash, it is completely decomposed, yielding paranitraniline. If boiled for $1\frac{1}{2}$ hours with alcoholic potash, or for half an hour with concentrated hydrochloric acid, it yields metanitroanthranilic acid (Hübner, *Annalen*, **195**, 21), from which different azo-dyes can be obtained.

Ethylic anthranilate hydrochloride, when mixed with concentrated potassium thiocyanate, yields a crystalline precipitate of the *thiocarbamide*, $COOEt\cdot C_6H_4\cdot NH\cdot CS\cdot NH_2$, which melts at 120—121°. If, however, the same compound is boiled for 40 hours with an excess of potassium thiocyanate solution, a white precipitate of *ketothiotetrahydroquinazoline*, $C_6H_4<\begin{matrix}CO\cdot NH\\ \vert\\ NH\cdot CS\end{matrix}$, is formed. This same compound is also obtained when the above-mentioned thiocarbamide is heated for 5 minutes at 125°.

Hübner's method (*Annalen*, **222**, 195) for the nitration of orthochlorobenzoic acid gives but poor yields, the best result being obtained by dissolving the chlorobenzoic acid (20 grams) in concentrated sulphuric acid (100 grams), and then slowly adding a mixture of 100 per cent. nitric acid (15 grams) and concentrated sulphuric acid (30 grams). Ethylic orthochlorometanitrobenzoate, melting at 28—29°, readily reacts with phenylhydrazine (4 mols.) when the mixture is warmed for several hours on the water bath, a mixture of nitrophenylindazolone and *ethylic nitrophenylhydrazidobenzoate* being formed. The latter crystallises in long, golden-yellow needles, melts at 129—130°, and is readily soluble in boiling alcohol. When hydrolysed with alkalis, it yields *nitrophenylindazolone*, $NO_2\cdot C_6H_3<\begin{matrix}CO\\NH\end{matrix}>NPh$, which crystallises from glacial acetic acid in small, yellowish-green needles; it decomposes above 260°, and is but sparingly soluble in the usual solvents. It readily dissolves in alkalis, yielding deep red solutions; the *sodium* derivative crystallises from concentrated caustic soda solution in red plates having a green lustre. J. J. S.

Melilotol. By Fritz Wischo (*Chem. Centr.*, 1896, ii, 540; from *Pharm. Post.*, **29**, 309—310).—By distilling dried, flowering *Melilotus*, and shaking the distillate with ether, Phipson obtained an oily product possessing an odour like *Melilotus*, and which he named melilotol. This substance, however, is a mixture of coumarin with a little melilotaldehyde, melilotic acid, $OH\cdot C_6H_4\cdot CH_2CH_2\cdot COOH$ [= 1 : 2], and its anhydride, which has an odour like that of coumarin. E. W. W.

Action of Ethylic Oxalate and Sodium Ethoxide on Nitrotoluenes. Synthesis of Nitrated Phenylpyruvic Acids. By Arnold Reissert (*Ber.*, 1897, **30**, 1030—1053).—Derivatives of benzene which contain a nitro-group in the ortho- or para-position relatively to a methyl group readily condense with ethylic oxalate in presence of sodium ethoxide, yielding nitrated phenylpyruvic acids. In each case, it is necessary to find out the most suitable conditions under which the action takes place.

Orthonitrophenylpyruvic acid, $NO_2\cdot C_6H_4\cdot CH_2\cdot CO\cdot COOH$. A solution

of the requisite quantities of sodium ethoxide, ethylic oxalate, and orthonitrotoluene, after being kept at 35—40° for three days, is carefully neutralised with the requisite quantity of 20 per cent. hydrochloric acid, great care being taken that the temperature does not rise. The acid and unaltered nitrotoluene are extracted with ether, and then separated by a 5 per cent. sodium hydroxide solution in which the acid is readily soluble, and can be precipitated again by hydrochloric acid in the form of an oil which slowly solidifies, and may then be recrystallised from benzene. It forms yellowish, glistening, bulky needles, sinters at 115°, melts at about 121°, and is readily soluble in hot water, in alcohol, ether, acetic acid or acetone, but only sparingly in benzene or chloroform. Solutions of the acid in caustic alkali have a deep reddish-brown colour; with alkali carbonates, the colour is not so deep. Aqueous solutions of the acid give a deep green coloration with ferric chloride. The *phenylhydrazone*,

$$NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}C(COOH){:}N_2HPh,$$

forms hard, yellow, prismatic crystals, melts and decomposes at 148—149°, and is readily soluble in solutions of alkalis or alkali carbonate.

When boiled with dilute sodium hydroxide, the acid is decomposed into orthonitrotoluene, isatin, and a small quantity of *diorthodinitrodibenzyl*, which melts at 122°. Nitrous acid converts the substituted pyruvic acid into carbonic anhydride and orthonitrobenzonitrile. If less than 2 molecules of nitrous acid are used for each molecule of the acid, a small quantity of *anhydro-β-oximidorthonitrobenzoyloxalic acid*, $O[N{:}C(C_6H_4{\cdot}NO_2){\cdot}CO{\cdot}COOH]_2$, is obtained as an oil; its *diphenylhydrazone* crystallises in deep yellow needles, and melts at 157°. Warm, concentrated sulphuric acid converts orthonitrophenylpyruvic acid into orthonitrophenylacetic acid, and the same product is obtained by the action of hydrogen peroxide. Potassium permanganate, both in acid and alkaline solution, yields a mixture of orthonitrobenzaldehyde and the corresponding acid. Chromic mixture yields orthonitrobenzaldehyde and orthonitrophenylacetic acid.

Orthonitrobenzylidene bromide, $NO_2{\cdot}C_6H_4{\cdot}CHBr_2$, obtained by th action of an alkaline solution of bromine on the acid, crystallises in large, colourless prisms, and melts at 46°. Bleaching powder converts the sodium salt of the nitro-acid into a compound, $C_{16}H_{12}N_2O_6$, which crystallises in long, yellowish, glistening needles, and melts at 160°. Indole-2′-carboxylic acid is obtained when orthonitrophenylpyruvic acid is reduced with zinc dust and acetic acid, but 1′-hydroxyindole-2′-carboxylic acid is formed when sodium amalgam is employed as the reducing agent. Indigo is formed when the latter acid is dissolved in concentrated sulphuric acid, the solution kept for 1—2 days at the ordinary temperature, then poured into water, and the solution saturated with ammonia and left exposed to the air in a flat dish for 1 to 2 days with constant stirring.

Paranitrophenylpyruvic acid crystallises from its acetic acid solution in hard, orange-yellow, glistening crystals, which contain 1 molecule of acetic acid; after drying, it melts at 194°. The acid is readily soluble in alcohol, ether, or acetone, and fairly readily in acetic acid, but only sparingly in water, benzene, and chloroform; its aqueous

solution gives a bluish-green coloration with ferric chloride. The *phenylhydrazone* crystallises in yellow needles, and melts with decomposition at 168°.

When oxidised with chromic mixture, the acid gave a small quantity of paranitrobenzaldehyde.

Orthonitroparamethylphenylpyruvic acid is obtained from nitroparaxylene when double the quantities of sodium ethoxide and ethylic oxalate required by theory are employed; it crystallises in almost colourless needles, melts at 145°, and yields a *phenylhydrazone* melting at 170°. When reduced with zinc dust and acetic acid, it yields 2-*methylindole-2′-carboxylic acid*, which crystallises from its aqueous solution in small needles melting at 217°. When heated above its melting point, the latter acid is converted into carbonic anhydride and metamethylindole.

1′-*Hydroxy-2-methylindole-2′-carboxylic acid* is obtained when orthonitrometamethylphenylpyruvic acid is reduced with sodium amalgam; it crystallises in needles and melts at 165°.

The author has also made attempts to condense 2 molecules of ortho- or para-nitrotoluene with 1 molecule of ethylic oxalate, but the products formed were the acids already mentioned, together with small quantities of orthodinitrodibenzyl and paradinitrodibenzyl.

J. J. S.

Homologues of α-Cyanobenzoylpropionic Acid. By C. Timothée Klobb (*Bull. Soc. Chim.*, 1897, [iii], **15**, 773—778).—The author has already shown that, in ethereal salts of acids of this type, the hydrogen atoms in the α-position can be replaced by sodium and subsequently by a hydrocarbon radicle, with formation of salts of the formula $COPh\cdot CH_2\cdot CR(CN)\cdot COOR'$. The paper contains an account of the action of potash on some of the ethereal salts of these acids, which have already been described.

α-Cyano-β-benzoyl-α-ethylpropionic acid, $COPh\cdot CH_2\cdot CEt(CN)\cdot COOH$, is a crystalline substance, insoluble in cold water, benzene, and chloroform, slightly soluble in hot water, and soluble in alcohol, xylene, and glacial acetic acid. It melts at 193°, and sublimes when heated. The sodium and barium salts were not obtained in the crystalline form. The silver salt crystallises from water in white crystals, which blacken when heated with water at 100°.

α-Cyano-β-benzoyl-α-methylpropionic acid is a white, crystalline substance which melts at 172°, and is very soluble in hot water, ether, alcohol, and acetic acid, slightly soluble in benzene and chloroform.

α-Cyano-β-benzoyl-α-propylpropionic acid forms white needles, soluble in water, alcohol, ether, and boiling xylene, insoluble in benzene, and melts at 189°.

α-Cyano-β-benzoyl-α-benzylpropionic acid melts at 178° and is insoluble in water, but soluble in alcohol, ether, and boiling xylene. The barium salt crystallises with $1H_2O$. M. W. T.

Action of Phenylhydrazine on Gallic Acid and on Dibromogallic Acid. By Alexandre Biétrix (*Bull. Soc. Chim.*, 1897, [iii], **15**, 783—786).—By the action of phenylhydrazine on a concentrated

solution of gallic acid, two compounds are formed; and on adding ether, crystals of the formula $C_6H_2(OH)_3\cdot CO\cdot NH\cdot NH_2Ph$ separate, which, after purification, are quite colourless, melt at 138—139°, and are very soluble in water and alcohol, but insoluble in chloroform. Its solutions give the characteristic blue with ferric chloride.

The alcohol ether solution, on standing, deposits a substance which, after recrystallisation, gives in solution no coloration with ferric chloride, indicating that no free hydroxyl groups are present. It is soluble in water, alcohol, and ether, but insoluble in chloroform. It decomposes at 185°, without melting, and from analysis has the formula $C_6H_2(NH\cdot NH_2Ph)_3\cdot CO\cdot NH\cdot NH_2Ph$.

Dibromogallic acid reacts in exactly the same way with phenylhydrazine. The monophenylhydrazine derivative, which separates on adding ether to the alcoholic solution, is soluble in water and alcohol but insoluble in ether and chloroform. It melts at 160° with decomposition, and gives the characteristic blue colour with ferric chloride. The tetraphenylhydrazide derivative resembles the corresponding derivative of gallic acid. It decomposes at 200°. M. W. T.

Norhemipinates, and the Author's Water of Crystallisation Theory. By THEODOR SALZER (*Ber.*, 1897, **30**, 1101—1104. Compare Freund and Horst, Abstr., 1894, i, 247).—Ammonium hydrogen hemipinate does not contain a molecule of water of crystallisation; if heated, however, between 135° and 180°, it yields an anhydride by the loss of $1H_2O$. The normal ammonium salt is difficult to prepare, as the solution loses ammonia on evaporation.

The barium salt crystallises with $1H_2O$, and not with $2H_2O$; the calcium salt could only be obtained in the form of a gelatinous mass, and no definite crystals containing $3H_2O$ could be prepared. The barium hydrogen salt, $Ba(C_8H_5O_6)_2$, crystallises with $3H_2O$, which it loses at 100—125°, and between 135° and 180° it loses two more molecules of water, yielding an anhydride. The calcium hydrogen salt resembles the corresponding barium salt.

These salts form exceptions to the author's general rule.

J. J. S.

Action of Sulphurous Anhydride on Aromatic Hydroxylamines. By W. BRETSCHNEIDER (*J. pr. Chem.*, 1897, [ii], **55**, 285—304). —The hydroxylamines were prepared by reducing the corresponding nitro-compounds with zinc dust in aqueous-alcoholic solution containing a little calcium chloride (Wohl, Abstr., 1894, i, 409); it was found advisable to pass carbonic anhydride through the apparatus, and sometimes to add ether, whereby the boiling point of the mixture was lowered. The hydroxylamine was dissolved in 60 per cent. alcohol, and the solution saturated with sulphurous anhydride, being cooled meanwhile; in many cases, where the yield of the hydroxylamine was small, this compound was never isolated, but the solution was merely filtered from the zinc, &c., and at once saturated with sulphurous anhydride.

Only phenylhydroxylamine and *paratolylhydroxylamine* (with $\frac{1}{2}H_2O$) were obtained in satisfactory amount. Most of the hydroxylamines

examined give amidosulphonic acids when treated with sulphurous anhydride, the yield being best at 10°, but some sulphate of the amine is formed in addition, no doubt by the action of water on a sulphonamic acid, which might be expected to be a primary product of the action. For example, $C_6H_5\cdot NH\cdot OH$ yields $SO_3H\cdot C_6H_4\cdot NH_2$ and $C_6H_5\cdot NH_2,H_2SO_4$ (from $C_6H_5\cdot NH\cdot SO_3H$). The sulphonic group goes in the ortho-position to the amido-group; for example, phenylhydroxylamine yields 1:2-amidosulphonic acid, 1:4-tolylhydroxylamine yields 4-amido-1-methylbenzene-3-sulphonic acid, and 1 : 2-tolylhydroxylamine yields 2-amido-1-methyl-3-benzenesulphonic acid. When both ortho-positions are already occupied, as in the case of metaxylylhydroxylamine [$NHOH:Me_2 = 2:1:3$], no action takes place. In the case of 1-naphthyl hydroxylamine, 1-amido-4-naphthalenesulphonic acid is formed.

With phenylmethylhydrazine, phthalylhydroxylamine (best prepared by warming phthalimide with hydroxylamine hydrochloride and a little alcoholic ammonia), and benzhydroxamic acid, sulphurous anhydride did not form a sulphonic acid. Paratoluenesulphinic acid reacts with phenylhydroxylamine when the two substances are heated together at 100° in alcoholic solution; the product melts at 142°, and probably has the constitution $C_6H_4Me\cdot SO_2\cdot NPh\cdot OH$, for it is decomposed by aqueous alkalis into paratoluenesulphinic acid and nitrosobenzene.

C. F. B.

Some Aromatic Amido-alcohols and their Derivatives. By Heinrich Kippenberg (*Ber.*, 1897, **30**, 1130—1141).—Several orthamido-alcohols were prepared by the reduction of the corresponding ketones, and it was noticed that whilst pure aromatic ketones, on treatment with sodium amalgam, yielded the alcohol, acetophenone and its derivatives were, for the most part, reduced to pinacones; thus, orthamidoacetophenone gave, on reduction, *orthodiamidoacetophenonepinacone*, $OH\cdot CMe(C_6H_4\cdot NH_2)\cdot CMe(C_6H_4\cdot NH_2)\cdot OH$, a substance crystallising from dilute alcohol, and melting at 169—170°; whilst orthamidophenyl paratolyl ketone, prepared by Hofmann's method, gave *orthamidophenylparatolylcarbinol*, $C_7H_7\cdot CH(OH)\cdot C_6H_4\cdot NH_2$, which crystallises from a mixture of benzene and light petroleum in silky, white needles melting at 99·5°; this hydrol reacts readily with thiocyanic acid, forming *4-paratolyltetrahydrothioquinazoline*,

$$C_6H_4<\begin{array}{l}CH(C_7H_7)\cdot NH\\ NH\text{———}CS\end{array},$$

which crystallises from alcohol in white needles melting at 224°, and with carbamide forms *4-paratolyltetrahydroketoquinazoline*,

$$C_6H_4<\begin{array}{l}CH(C_7H_7)\cdot NH\\ NH\text{———}CO\end{array},$$

crystallising in microscopic prisms melting at 208—209°. On heating a mixture of equal parts of the ketone and carbamide at 180—190°, *4-paratolyldihydroketoquinazoline*, $C_6H_4<\begin{array}{l}C(C_7H_7):N\\ NH\text{——}CO\end{array}$, is formed; this separates from hot alcohol in greyish-yellow prisms melting at 286°.

Paramidobenzophenone, on reduction, yields *paramidobenzhydrol*, $NH_2\cdot C_6H_4\cdot CHPh\cdot OH$, which crystallises from hot water in long, white needles melting at 121°; on treatment with cold, dilute acetic acid, it gives a very insoluble compound, melting and decomposing at

220—225°, probably *paramidobenzhydrol anhydride* $(NH\cdot C_6H_4\cdot CHPh)_x$. On dissolving paramidobenzhydrol in dilute hydrochloric acid, and saturating the solution with hydrogen sulphide, the hydrochloride of *aa-diphenyldiparamidobenzylic sulphide*, $S(CHPh\cdot C_6H_4\cdot NH_2,HCl)_2 + H_2O$, was produced, melting at 263°, and on treating it with dimethylaniline, water was eliminated and it was converted into *dimethyldiparamidotriphenylmethane*, $NMe_2\cdot C_6H_4\cdot CHPh\cdot C_6H_4\cdot NH_2$; this melts at 117—118°. J. F. T.

Action of Aluminium Chloride on the Chlorides of Dicarbodiphenylimide. By HERBERT N. McCOY (*Ber.*, 1897, **30**, 1090—1094).—When a solution of carbodiphenylimide in benzene is saturated with hydrogen chloride, then diluted with carbon bisulphide, and digested with aluminium chloride, it is converted into a substance which has the composition and molecular weight corresponding with a dimolecular *polymeride*, $C_{26}H_{20}N_4$.

This substance exists in two forms, one of which crystallises in sulphur-yellow needles melting at 171°, whilst the second melts at 184°, and is formed when the first is heated to its melting point and then allowed to cool. Both compounds dissolve readily in dilute hydrochloric acid, forming a yellow solution, which becomes colourless on boiling. Alkalis then precipitate a white *compound*, $C_{20}H_{15}N_3O$, which crystallises in colourless needles melting at 163°, whilst aniline remains in solution. The constitution of these isomerides has not yet been determined, but it appears very improbable that they are simply symmetric polymerides. A. H.

Ethylic Diphenylacetoacetate. By JAKOB VOLHARD (*Annalen*, 1897, **296**, 1—33).—Wislicenus has shown that, under the influence of sodium ethoxide, ethylic phenylacetate combines with ethylic oxalate in molecular proportion, yielding ethylic phenylacetoxalate; in attempting to induce the combination of ethylic phenylacetate with two molecular proportions of ethylic oxalate, the author has obtained ethylic diphenylacetoacetate, $CH_2Ph\cdot CO\cdot CHPh\cdot COOEt$, which is formed by the elimination of ethylic alcohol from two molecular proportions of the ethereal salt.

Ethylic diphenylacetoacetate, $CH_2Ph\cdot CO\cdot CHPh\cdot COOEt$, is prepared by agitating ethylic phenylacetate (65 parts) with sodium ethoxide (27·5 parts) which has been prepared from anhydrous alcohol and dried in hydrogen at 200°; the liquid is then heated on the water bath for half an hour after the sodium ethoxide has dissolved, rapidly cooled, and the solid product dissolved in water and acidified with acetic acid. The salt crystallises from alcohol in lustrous, colourless needles, and melts at 78—79°; it is insoluble in water, but dissolves readily in the usual organic solvents. Prolonged treatment with a boiling solution of barium hydroxide converts it into phenylacetic acid; an alcoholic solution yields the blue, crystalline, *copper* derivative when treated with copper acetate. The *oxime* separates from alcohol in compact, colourless crystals, and melts at 112—113°; when dissolved in concentrated sulphuric acid, it undergoes partial conversion into phenylbenzylisoxazolone.

Phenylbenzylisoxazolone, $\begin{matrix} N\!:\!C(CH_2Ph) \\ | \qquad\qquad \\ O\text{———}CO \end{matrix}\!\!>\!CHPh$, produced along with

the oxime when hydroxylamine acts on ethylic diphenylacetoacetate, crystallises in lustrous needles melting at 106—107°; the *silver* derivative is crystalline, and the *aniline*, *toluidine*, and *phenylhydrazine* salts melt at 112—113°, 116—118°, and 118—119° respectively. An alcoholic solution of phenylbenzylisoxazolone develops an intense green coloration with ferric chloride, the *compound*, $C_{32}H_{24}N_2O_5$, which crystallises in colourless, six-sided plates, and melts at 148—149°, being also produced; this substance, unlike phenylbenzylisoxazolone, is quite insoluble in alkalis.

Phenylbenzylpyrazolone, $\begin{matrix}NH\cdot C(CH_2Ph)\\ | \qquad\qquad\quad \\ NH\text{———————}CO\end{matrix}\!\!>\!CPh$, arises from the action of hydrazine hydrate on ethylic diphenylacetoacetate, and crystallises from alcohol in tufts of slender needles containing 1 mol. of the solvent. After the first crystallisation, the melting point is 125—126°, but is raised to 141° by recrystallisation from toluene, and if the substance is again crystallised from alcohol, it melts at 172°. The *methyl* derivative crystallises from methylic alcohol, in which it is sparingly soluble, and melts at 237—238°.

Diphenylbenzylpyrazolone, $\begin{matrix}NPh\cdot C(CH_2Ph)\\ | \qquad\qquad\quad \\ NH\text{———————}CO\end{matrix}\!\!>\!CPh$, prepared by heating ethylic diphenylacetoacetate with phenylhydrazine in glacial acetic acid, crystallises from much hot alcohol in slender, white needles. It dissolves more readily in glacial acetic acid, and melts at 231—232°. The *methyl* derivative crystallises from alcohol.

Concentrated sulphuric acid eliminates alcohol from ethylic diphenylacetate, converting it into a derivative of naphthalene; this change is analogous to the production of naphthol or its derivatives from phenylisocrotonic, phenylparaconic, or benzylidenelevulinic acid. The exact nature of the naphthalene derivative must, for the present, remain undecided, as some of its properties appear to be consistent with a ketonic structure, whilst in other respects it is hydroxylic in character; oxidation converts it into a quinhydrone, which then passes into a hydroxyquinone. The latter, when distilled with zinc dust, yields β-phenylnaphthalene.

1 : 3 : 2-*Dihydroxyphenylnaphthalene* is obtained by dissolving ethylic diphenylacetoacetate in 10 parts of concentrated sulphuric acid; it crystallises from chloroform in colourless, six- or eight-sided plates, and melts at 165—166°. It becomes pink when exposed to the air, and ferric chloride develops a deep red coloration. The *diacetyl* derivative separates from alcohol in lustrous, white, prismatic crystals, and melts at 136—137·5°.

1 : 2-*Hydroxyphenyl-β-naphthaquinone*, or 3 : 2-*hydroxyphenyl-α-naphthaquinone*, is prepared by passing air for 24 hours through a solution of 1 : 3 : 2-dihydroxyphenylnaphthalene in caustic soda; it crystallises from alcohol in long, yellow needles, and melts at 146—147°. It dissolves readily in ammonia, alkalis, and alkali carbonates, forming reddish-brown solutions; concentrated sulphuric acid dissolves it with a brownish coloration, becoming green, and finally intensely blue when the solution is agitated with benzene containing thiophen. The *silver* derivative, which is crystalline, and brownish-red, dissolves readily in alcohol and water; the *methyl* ether separates from methylic alcohol

in compact, brownish-yellow crystals, and melts at 122—123°. The *acetate* melts at 112—113·5°, and the *phenylhydrazone* crystallises from alcohol in prismatic needles, and melts, decomposing, at 200°; the *hydrazone* is brownish-yellow and crystalline, and the *oxime* separates from alcohol in yellow needles melting at 215—216°, when it decomposes. Both the oxime and phenylhydrazone develop intense coloration with ferric chloride.

Phenylhydroxynaphthaphenazine, $\begin{array}{l}C(OH)\cdot C_6H_4\cdot C:N \\ CPh\text{———————}C:N\end{array}\!\!>C_6H_4$, or $\begin{array}{l}CO\cdot C_6H_4\cdot C{=}N \\ CPh\text{———}C\cdot NH\end{array}\!\!>C_6H_4$, obtained by heating the hydroxyquinone with alcoholic orthophenylenediamine, crystallises from chloroform in reddish-violet needles melting at 229—231°; the *sodium* derivative crystallises in beautiful, long, red needles, exhibiting greenish, metallic surface lustre, and the *silver* derivative is violet. The *acetyl* derivative crystallises in lustrous, yellowish needles, and melts at 262—262·5°.

Phenylhydroxynaphthaquinhydrone, $C_{16}H_{11}O_2\cdot O\cdot C_{16}H_{11}O_2$, is the intermediate product in the conversion of the hydroxynaphthol into the hydroxyquinone, and separates from the mother liquor on adding light petroleum to it; it is more conveniently prepared, however, by passing air for 12—14 hours through a solution of the hydroxynaphthol in alcoholic ammonia, and is thus obtained in lustrous, red crystals melting at 171·5—172·5°. The *silver* derivative is bluish-red.

The *compound*, $C_{32}H_{20}O_6$, is obtained on oxidising hydroxyphenylnaphthaquinone in alcoholic solution with ferric chloride; it dissolves sparingly in alcohol and glacial acetic acid, but crystallises from aniline or nitrobenzene in reddish-brown needles, and melts at 278—280°. M. O. F.

Oxidation of the Rosanilines by Lead Dioxide. By MAURICE PRUD'HOMME (*Bull. Soc. Chim.*, 1897, iii, 15, 780—783).—The author contradicts Rosensthiel's statement (this vol., i, 225) that the colour of the rosaniline bases precipitated from solution by alkalis is due to the adherence of some of the salt.

The changes which 'patent blue' or metahydroxy-malachite green undergoes when oxidised are compared with those which take place on oxidation of other rosaniline dyes. When oxidised in acid solution by lead dioxide, 'patent blue' appears to be the only member of the class which does not give an alkylated benzidine; on adding lead peroxide and acetic acid to the precipitated base, however, it appears to behave in the usual manner. M. W. T.

Flavone Derivatives. V. Ketocumaran and some of its Condensation Products. By PAUL FRIEDLÄNDER and JULIUS NEUDÖRFER (*Ber.*, 1897, 30, 1077—1083).—Orthohydroxyacetophenone, which is best prepared from nitrophenylacetylene, readily yields the acetate when it is heated at 150° with acetic anhydride. The acetate is converted by bromination in solution in carbon disulphide into *acetoxyacetophenone bromide*, $OAc\cdot C_6H_4\cdot CO\cdot CH_2Br$, which crystallises in long, white needles melting at 67°. When the latter is boiled with chalk

and water, it is converted into *ketocumaran*, $C_6H_4<^{O}_{CO}>CH_2$, which crystallises in white needles, melts at 97°, and dissolves in aqueous soda but is reprecipitated by acids; when the alkaline solution is warmed, decomposition occurs and salicylaldehyde is produced. On treatment with alkaline oxidising agents, such as Fehling's solution, it is converted into a blue compound, which will form the subject of a separate communication. Ketocumaran and orthohydroxyacetophenone bromide readily react with aldehydes to form flavone derivatives. *Flavone*, $C_{15}H_{10}O_2$, is formed by the condensation of ketocumaran with benzaldehyde, and separates in almost colourless crystals melting at 108°; it gives an orange-yellow coloration with sulphuric acid, and is insoluble in aqueous soda in the cold, but is decomposed on heating. *Dihydroxyflavone*, $C_{15}H_{10}O_4$, obtained when protocatechuic aldehyde is employed, forms brownish-yellow needles melting at 224°; it gives a bluish-violet coloration with concentrated aqueous soda, and an orange coloration with sulphuric acid. The *acetate* melts at 134°. *Methylenedihydroxyflavone*, $C_{16}H_{10}O_4$, is prepared from piperonal, and forms deep yellow needles melting at 192°. It is insoluble in alkalis, and gives an eosin red coloration with sulphuric acid.

A comparison of the different flavone derivatives shows that the position of the hydroxyl groups has a great influence on the colorations which they yield with sulphuric acid and with aqueous soda. A. H.

3′ : 4′-Dihydroxybenzylideneindanedione. By STANISLAUS VON KOSTANECKI (*Ber.*, 1897, **30**, 1183—1186. Compare Abstr., 1896, i, 606).—3′ : 4′-*Dihydroxybenzylideneindanedione*,

$$C_6H_4<^{CO}_{CO}>C:\overset{1'}{C}H\cdot C_6H_3\overset{3':4'}{(OH)_2},$$

prepared by heating protocatechuic aldehyde with indanedione in molecular proportion at 110—120°, and crystallises from alcohol in brownish-yellow needles; it sublimes in small, yellow needles, and melts and decomposes at 257°. The solution in alkalis is reddish-violet, finally becoming brownish-yellow; with alum mordants, it behaves as a yellow colouring matter. The *diacetyl* derivative crystallises in yellowish prisms, and melts at 186°. The *methylenic ether* is prepared from indanedione and piperonaldehyde; it crystallises from pyridine in magnificent, intensely yellow needles, and melts at 209°. The *monomethylic ether*, obtained from indanedione and vanillin, crystallises in long, yellow needles melting at 212°; the *acetyl* derivative of the monomethyl ether melts at 184—185°. M. O. F.

Condensation Products of Cyclic Ketones III. By OTTO WALLACH (*Ber.*, 1897, **30**, 1094—1096. Compare Abstr., this vol., i, 159).—When cyclopentanone is saturated with hydrogen chloride and allowed to remain for several weeks, it yields, on distillation, unaltered cyclopentanone, dicyclopentenepentanone, $C_{10}H_{14}O$, and *tricyclotrimethylenebenzene*,

$$CH_2<\begin{matrix}CH_2\cdot C:C & \overset{CH_2\cdot CH_2\cdot CH_2}{———} & C:C\cdot CH_2 \\ CH_2\cdot C & ═════ & C\cdot CH_2\end{matrix}>CH_2.$$

The last of these compounds forms brittle, colourless crystals melt-

ing at 96—97°, and is not attacked by dilute potassium permanganate, but is readily oxidised by dilute nitric acid and by chromic acid. It has a molecular weight corresponding with the above formula, and is apparently formed from the pentanone in the same way as mesitylene from acetone. A. H.

Naphthalene Tetrabromide. By WILLIAM R. ORNDORFF and C. B. MOYER (*Amer. Chem. J.*, 1897, **19**, 262—270).—*Naphthalene tetrabromide* may be prepared by the gradual addition of bromine to well-cooled naphthalene mixed with a small quantity of sodium hydroxide. The deep red, pasty mass was purified by repeated treatment with small quantities of lukewarm alcohol, which extracted unchanged naphthalene, α-monobromonaphthalene, and 1 : 4-dibromonaphthalene; the residue was recrystallised several times from chloroform, when transparent, monoclinic prisms were obtained, which became opaque on exposure to light, or when heated. The crystals melt and decompose at 111°, are insoluble in water, ether, glacial acetic acid, and cold alcohol, but readily soluble in carbon bisulphide, light petroleum, hot chloroform, and benzene.

The yield was very small, but although the process was modified in various ways, it could not be improved, nor could any other tetrabromide be isolated.

Attempts to separate a stereoisomeride from this tetrabromide proved unsuccessful.

When heated to several degrees above its melting point, bromine and hydrogen bromide are given off, 1 : 4-dibromonaphthalene and a monobromonaphthalene being formed. On boiling with alcoholic potassium hydroxide, it is completely decomposed, the product consisting mainly of a bromonaphthalene. On oxidation with nitric acid, the only product identified was phthalic acid.

Attempts to determine the molecular weight of the tetrabromide by the boiling point method proved unsuccessful owing to decomposition, even when substances with such low boiling points as chloroform and carbon bisulphide were used. A. W. C.

Derivatives of Dihydroxynaphthalene. By RUDOLF NIETZKI and TH. KNAPP (*Ber.*, 1897, **30**, 1119—1124. Compare Clausius, Abstr., 1890, 627).—2′ : 1 : 2-*Hydroxynaphthaquinonedioxime*,

$$OH \cdot C_{10}H_5(N \cdot OH)_2,$$

obtained when an alcoholic solution of the monoxime described by Clausius is boiled with hydroxylamine hydrochloride, crystallises from dilute acetic acid in light, orange-coloured needles, melts at 195°, and is readily soluble in alcohol, ether, ethylic acetate, and acetic acid. The dioxime readily yields an internal anhydride; on warming with concentrated potash, crystals of the *potassium* salt of this anhydride are formed. On decomposing the potassium salt with hydrochloric acid, the anhydride, *β-naphtholfurazan*, is obtained; this crystallises from alcohol in long, colourless needles melting at 213—214°. If the dioxime is warmed with acetic anhydride, the *acetyl* derivative of β-naphtholfurazan is obtained; this forms silky needles, melts at 137°, and on hydrolysis yields the furazan. *Trinitrodinitroso-β-naphthol*, obtained by the action of nitric acid (sp. gr. 1·4) on a mixture

of the dioxime and glacial acetic acid, forms a sparingly soluble *potassium* salt, crystallising in orange-yellow plates, and exploding when heated to 260°. To prepare the pure free naphthol, the potassium salt is dissolved in fuming nitric acid and water added; it forms glistening, rhombic, yellow crystals, melts at 208°, and explodes at a slightly higher temperature. Its *ethylic* ether crystallises in pale yellow needles, melts at 167°, and is readily soluble in benzene.

Dinitrodinitroso-β-naphthol, obtained by the action of nitric acid on the dioxime and glacial acetic acid in the cold, crystallises in yellow needles, and melts at 196°; its *potassium* salt crystallises in small, red needles, and is moderately soluble in water.

Trinitro-β-naphtholfurazan is obtained when the acetyl derivative of β-naphtholfurazan is nitrated with fuming nitric acid. It crystallises from toluene in orange-coloured, glistening needles, which contain toluene of crystallisation. It is readily soluble in alkalis, and forms a sparingly soluble *barium* salt.

When amidodihydroxynaphthalene, obtained by the reduction of nitrosodihydroxynaphthalene (Clausius, *loc. cit.*), is warmed with anhydrous sodium acetate and acetic anhydride, it yields a *triacetyl* derivative melting at 183°, but if the heating is continued, a *tetracetyl* derivative, $C_{10}H_5(OAc)_2 \cdot NAc_2$ [= 2′ : 2 : 1], which melts at 135°, is formed. The authors find that Clausius' 1 : 2 : 2′-hydroxynaphthaquinone crystallises in brown needles and melts at 194°. When the dioxime described above is carefully reduced with stannous chloride and hydrochloric acid, diamido-β-naphthol hydrochloride $[(NH_2)_2 : OH = 1 : 2 : 2']$ is obtained; it yields a *triacetyl* derivative melting at 244—245°.

J. J. S.

Derivatives of Anthracene and of Anthraquinone. By Carl Graebe and Siegfried Blumenfeld (*Ber.*, 1897, **30**, 1115—1119. Compare Graebe and Leonhardt, Abstr., 1896, i, 437).—*Methylic anthraquinone*-1-*carboxylate* forms pale yellow crystals and melts at 189°. The *amide* of anthraquinone-1-carboxylic acid, obtained by passing dry ammonia into a benzene solution of the chloride, crystallises from alcohol and melts at 280°. 1-*Amidoanthraquinone* was obtained by the action of bromine and potash on the amide, and is identical with the compound described by Römer, but has not the properties ascribed to it by Böttger and Petersen. The acetyl derivative of the base melts at 215° (corr.) and not at 202°, as stated by Römer. 1-Nitroanthraquinone melts at 228° (corr.); Böttger and Petersen give 230°, and Römer gives 220°.

Anthraquinone-1-carboxylic acid, when reduced with zinc dust and ammonia, yields an anthracene-1-carboxylic acid melting at 245°; this is probably identical with the acid described by Liebermann and Rath (*Ber.*, 1875, **8**, 246) as melting at about 260°. The *amide* melts at 260°, and crystallises in pale yellow plates; it is not readily decomposed when heated with dilute soda. J. J. S.

Terpenes and Ethereal Oils. By Otto Wallach (*Annalen*, 1897, **296**, 120—133. Compare Abstr., 1894, i, 337).—Attention has been drawn (*loc. cit.*) to the resemblance between menthonitrile and its derivatives, and certain compounds of the citronellic series; it is now shown that, through the nitrile, menthone is convertible into open

chain compounds, a process which gains interest from the fact that the converse change, namely, production of pulegone from citronellaldehyde, has been accomplished recently (Tiemann and Schmidt, this vol., i, 198).

Menthonenic (decenoic) *acid*, $C_9H_{17}\cdot COOH$, is produced on hydrolysing menthonitrile with sodium ethoxide in sealed tubes at 120°; it boils at 257—261°, has the sp. gr. = 0·918, and the refractive index $n_D = 1·45109$ at 20°. Oxidation with potassium permanganate gives rise to β-methyladipic acid, the substance which Tiemann and Schmidt obtained from citronellic acid by the same process (Abstr., 1896, i, 383); in spite of the resemblance between citronellic and menthonenic acids, however, close comparison shows that they are not identical, this being probably due to the different situation of the ethylenic linking.

A *decoic acid*, $CHMe_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CHMe\cdot CH_2\cdot COOH$, is prepared by heating menthoneoxime (10 grams) with caustic potash (10 grams) and water (2 c.c.) at 220—230° for an hour, and boils at 249—251°; it has the sp. gr. = 0·905, and the refractive index $n_D = 1·4373$. The *amide* crystallises from water, and melts at 108—109°.

When menthonitrile is reduced, two bases are obtained, menthonylamine, $C_{10}H_{19}NH_2$, and hydroxyhydromenthonylamine, $OH\cdot C_{10}H_{20}\cdot NH_2$, which is not volatile in steam (Abstr., 1894, i, 338); the alcohol produced by the action of nitrous acid on the former base is called *menthocitronellol* by the author, and has the constitution

$$CMe_2{:}CH\cdot CH_2\cdot CH_2\cdot CHMe\cdot CH_2\cdot CH_2\cdot OH,$$

ascribed by Tiemann and Schmidt to natural citronellol (Abstr., 1896, i, 383). *Dimethyloctylene glycol* (2 : 6-*dimethyloctane*-2 : 8-*diol*),

$$OH\cdot CMe_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CHMe\cdot CH_2\cdot CH_2\cdot OH,$$

is obtained in the same way from hydroxyhydromenthonylamine, and boils at 153—156° under a pressure of 19 mm.; dilute sulphuric acid converts it into menthocitronellol.

Menthocitronellaldehyde, $C_9H_{17}\cdot COH$, prepared by oxidising the alcohol with chromic acid, boils at 86—88° under a pressure of 16 mm. and at about 200° under atmospheric pressure; it has the sp. gr. = 0·8455, and the refractive index $n_D = 1·43903$ at 20°. The citronellal-β-naphthocinchonic acid obtained by condensation with β-naphthylamine and pyruvic acid melts at 214—215°, and is therefore different from the compound with natural citronellaldehyde, which melts at 225° (Doebner, Abstr., 1894, i, 261). The semicarbazone is optically inactive, and melts at 89° (compare Tiemann and Schmidt, this vol., i, 199). M. O. F.

Oil of Levisticum officinale. By R. Braun (*Arch. Pharm.*, 1897, **235**, 1—19).—Oil of lovage has the characteristic taste and odour of Levisticum root. Its sp. gr. varies somewhat, the mean value = 1·0407 at 15°, and its refractive index = 1·5336—1·5337. It is readily soluble in alcohol (96 per cent.), ether, light petroleum, chloroform, acetic acid, &c. Iodine has no action, but bromine converts the oil into a resinous mass; potassium also acts violently, and on the addition of water an orange-red emulsion is obtained. When warmed with platinic chloride, an odour of angelic acid is developed. The oil begins to boil at about 170°, but at 200° decomposition ensues; it

was therefore distilled under diminished pressure, and the following fractions collected: (1) to 130°; (2) 130—176°, mostly 170—176°; (3) 200—250°, coloured brown; (4) 250—300°, coloured green; (5) 300—360°, dark green. These temperatures are calculated to normal pressure. Fraction 5 solidified on cooling, and was found to contain benzoic acid. Fractions 1, 3, and 4 were very small, and could not be investigated. Fraction 2 was found to contain two compounds. One of these, $C_{10}H_{18}O$, boils at 178°, has a sp. gr. = 0·9176 at 15°, and a refractive index = 1·4825; in its physical properties, it resembles cineol, but does not yield crystalline additive compounds with hydrogen chloride or with bromine. The second compound, $C_{10}H_{16}$, is best obtained by the prolonged action of alcoholic potash (30 per cent.) on the compound, $C_{10}H_{18}O$. It is a clear, colourless oil, with an odour resembling that of thyme; it boils at 176°, has a sp. gr. = 0·8534 at 15°, and a refractive index = 1·4777; it is dextrorotary (+5°), and in many respects resembles limonene, but yields no crystalline additive compound with bromine. A resinous substance was also obtained by the action of alcoholic potash on the compound $C_{10}H_{18}O$. When fused with potash, acetic, isovaleric, and benzoic acids were found among the products formed.

The oil from fresh roots appears to differ in some of its physical constants from the oil from the dried roots. The green roots also, on distillation, yield little or no resin. J. J. S.

French Oil of Basil. By JUSTIN DUPONT and JACQUES GUERLAIN (*Compt. rend.*, 1897, **124**, 300—302).—This oil, obtained by distilling the leaves of *Ocymum basilicum* with water, has a yellowish colour and a strong characteristic smell. It has a sp. gr. = 0·9154 at 15°, and a rotation of −7° 40′ in a 100 mm. tube. When distilled under atmospheric pressure, four-fifths pass over between 190—220°, a brown resinous mass remaining in the distilling flask, and on further fractionation, two main fractions are obtained, the one boiling at 195—200°, the other at 205—215°. The former is an oily, refractive liquid possessing the odour of lævorotatory linalol, and having the formula $C_{10}H_{18}O$; the following properties are recorded: sp. gr. = 0·8552 at 15°; $[\alpha]_D = -14·03°$; index of refraction, $n_D = 1·4565$; molecular refraction = 49. It combines with 4 atoms of bromine, giving an uncrystallisable liquid product, and, on heating with acetic anhydride, an *acetate* boiling at 128° (14 mm.), which, on saponification with alcoholic potash, yields geraniol, boiling at 115—117° (15 mm.). This fraction, therefore, consists of lævorotatory *linalol*. The fraction boiling at 205—215° had the odour of estragol, and exhibited a rotation of −6° 40′ in a 100 mm. tube. Even after treatment with alcoholic potash, in order to free it from ethers, and further fractionation, it was found impossible to obtain a product of definite composition. Its odour, its boiling point, and the formation of methylic iodide on treatment with hydriodic acid, having rendered it probable that this fraction consisted chiefly of estragol, it was heated with concentrated alcoholic potash for 24 hours, and after treatment with water and extraction with ether, the product was fractionally distilled. The main fraction, boiling at 225—230°, instantly solidified on the addition of a crystal of anethol, and melted, after drying between filter paper,

at 21°. The second fraction, therefore, of the oil consisted of *estragol* (paramethoxyallylbenzene). A. C. C.

$\beta\beta$-Dicamphor. By GIUSEPPE ODDO (*Gazzetta*, 1897, **27**, i, 149—194. Compare Abstr., 1894, i, 201).—On heating bromocamphor with sodium and toluene in a reflux apparatus on an oil bath, reduction occurs suddenly; after heating for 5 hours, water is added, and the toluene and aqueous solutions are distilled separately in a current of steam. Toluene, borneol, and camphor distil from the toluene solution, leaving a crystalline mass, which, on recrystallisation from alcohol and a mixture of petroleum and benzene, yields dicamphanhexane-1 : 4-dione, whilst the aqueous solution remaining in the distilling flask, when evaporated to dryness and crystallised from acetic acid, yields $\beta\beta$-dicamphor. The original aqueous washings, after being freed from volatile products by a current of steam, diluted, and acidified, yield a mixture of α-camphandioic anhydride, β-*trans*-dicamphandioic acid, and camphanonedicamphanonic acid, which are separated by treatment with soda and acid and crystallisation from alcohol.

I.—$\beta\beta$-*Dicamphan*-1 : 4-*dione* ($\beta\beta$-dicamphor), $\begin{array}{l}C_7H_{13}\cdot CH—CH\cdot C_7H_{13} \\ \;\;| \quad\;\;\;\; | \quad\;\;\;\; | \quad\;\;\; | \\ \;\;CH — CO \quad CO\cdot CH\end{array}$,
can also be prepared by reducing dicamphanhexane-1 : 4-dione or dicamphenehexadiene peroxide with zinc dust and acetic acid in alcoholic solution; it crystallises in colourless prisms melting at 165—166°, has the normal molecular weight in freezing benzene, and was previously termed dicamphoryl (Abstr., 1894, i, 202). In a 5 per cent. benzene solution at 27°, it has a specific rotation of $[\alpha]_D = -28\cdot4°$, whilst in a 25 per cent. absolute alcoholic solution at 22°, $[\alpha]_D = -4\cdot69°$; it is odourless, boils and decomposes at above 350°, and reacts with fuming hydrochloric acid at 150°. The *phenylhydrazone*, $C_{26}H_{36}N_2O$, crystallises in lustrous, white scales melting at 142—145°, and readily undergoes hydrolysis.

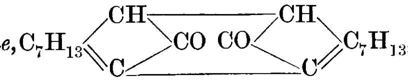
Dicamphandihydropyridazine (dicamphanazine),

$$C_8H_{14}\!\left\langle\begin{array}{c}CH \quad HC \\ | \qquad\;\; | \\ C{:}N\cdot N{:}C\end{array}\right\rangle\! C_8H_{14},$$

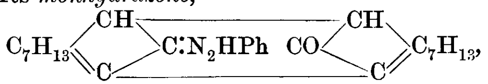
is prepared by boiling $\beta\beta$-dicamphor with hydrazine hydrochloride in acetic acid solution; it crystallises in colourless, lustrous scales melting at 155—156°, has the normal molecular weight in freezing benzene, and in a 5 per cent. benzene solution at 22° has a specific rotation of $[\alpha]_D = +118\cdot8°$. The *hydrochloride*, $C_{20}H_{30}N_2,HCl$, crystallises in white needles which do not melt at 265°, and the *picrate*, $C_{20}H_{30}N_2,C_6H_3N_3O_7$, in yellow needles which decompose at 200—205°; it is hydrolysed by boiling water. The *methiodide*, $C_{20}H_{30}N_2,MeI$, is prepared by heating the base with methylic iodide, and crystallises in white, prismatic needles melting at 207—208°. A *substance* crystallising in lustrous, white scales melting at 146—147° is also obtained in the preparation of dicamphanazine.

By the reduction of dicamphenehexadiene peroxide with zinc and acetic acid, a mixture of $\beta\beta$-dicamphor and *isodicamphor* is obtained; the latter could not be satisfactorily purified, and melts at 90—95°. It contains only one oxygen atom replaceable by hydrazine with formation of a *base*, $C_{10}H_{15}O\cdot C_{10}H_{15}\cdot N_2H_2$, which crystallises in lustrous,

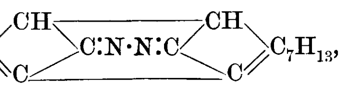
white scales melting at 165—166°; it is readily hydrolysed by hot hydrochloric acid, and shows very feeble reducing properties towards Fehling and alcoholic silver nitrate solutions.

II.—*Dicamphanhexane*-1:4 *dione*, 

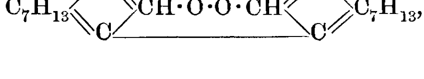
is prepared by fusing ββ-dicamphor with caustic potash at 200°, extracting the product with water, and crystallising the residue; it is also obtained during the treatment of bromocamphor with sodium, as described above. It crystallises in beautiful, yellow needles or plates melting at 192—193°, has the normal molecular weight in freezing benzene, and is very soluble in organic solvents; its specific rotation in a 3·5 per cent. benzene solution at 27° is $[\alpha]_D = +331°$, and in a 2·9 per cent. absolute alcoholic solution at 24°, $[\alpha]_D = +381°$. It distils at 332—335°, being completely converted into the isomeric dicamphenehexadiene peroxide; the same change occurs, although less completely, on heating with acetic anhydride or hydrochloric acid at 200—230°. Its *monhydrazone*,



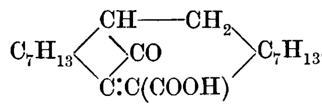
crystallises in lustrous, red scales melting at 117—118°; when dissolved in hot, dilute sulphuric acid, repeatedly crystallised from alcohol, or by prolonged boiling with water, it is converted into *isodicamphor*-1-*one*-4-*hydrazone*, $C_{20}H_{34}N_2O$, which crystallises in small, yellow needles melting at 177—178°.

Dicamphanhexaneazine,  is obtained in theoretical yield on boiling the dione with hydrazine hydrochloride in acetic acid solution; it crystallises in lustrous, white scales melting at 201—202°, has the normal molecular weight in freezing benzene, and has a specific rotation of $[\alpha]_D = +52·6°$ in a 5 per cent. benzene solution at 27°. It has a bitter taste and is physiologically very active. Its *hydrochloride*, $C_{20}H_{28}N_2,HCl$, crystallises in white needles melting at 230—235°, and its *picrate*, $C_{20}H_{28}N_2,C_6H_3N_3O_7$, in small, yellow prisms melting at 237° with decomposition; the *aurochloride*, $C_{20}H_{28}N_2,HAuCl_4$, crystallises in beautiful, yellow prisms melting and decomposing at 195—199°, and the *platinochloride*, $C_{20}H_{28}N_2,HCl,PtCl_4$, crystallises in red prisms decomposing at 260°. The *methiodide*, $C_{20}H_{28}N_2,MeI$, crystallises in beautiful, white needles melting at 201—202°; when treated with moist silver oxide in aqueous solution, it yields *dicamphanhexaneazinemethylammonium hydroxide*, $C_{20}H_{28}N_2,MeOH$, which crystallises in deliquescent, white needles and is a powerful base. Its *aurochloride*, $C_{20}H_{28}N_2,MeAuCl_4$, crystallises in scales melting at 200—202°, its *chloride*, $C_{20}H_{28}N_2,MeCl$, in white needles melting at 170° with decomposition, whilst its *nitrate* separates from water in small, white crystals which decompose at 210°.

Dicamphenehexadiene peroxide (dicamphoquinone),



may be prepared by the methods indicated above, or by treating the mixture obtained by the action of sodium on bromocamphor first with carbonic anhydride and then with water; it crystallises in beautiful, yellow scales melting at 155—156°. It has a specific rotation of $[\alpha]_D = +296{\cdot}2°$ in a 3·5 per cent. benzene solution at 16° and of $[\alpha]_D = +345{\cdot}3°$ in a 2·9 per cent. absolute alcohol solution at 15°; it is noteworthy that the difference between the specific rotations in benzene and alcohol is the same for both the peroxide and the isomeric dione. The latter does not combine with bromine, whilst the peroxide readily takes up 4 atoms of bromine giving an unstable product, but it does not react with phenylhydrazine or hydroxylamine, and only gives traces of dicamphanhexaneazine with hydrazine hydrochloride. The peroxide is not acted on by acetic anhydride or phenylcarbimide at 220—230°, although partial decomposition occurs; it is reduced by zinc and acetic acid to a mixture of ββ-dicamphor and isodicamphor, and is converted into the isomeric dione by treatment with sodium in toluene solution.

III.—*Camphanonecamphanonic acid*, 

crystallises in colourless, transparent, monosymmetric plates [$a:b:c = 0{\cdot}9407:1:0{\cdot}6065$. $\beta = 87°\ 11'$] melting at 224—225°; it has the normal molecular weight in freezing acetic acid, but in benzene solutions approximately double the normal values are obtained. In a 4·7 per cent. absolute alcohol solution at 12·6°, it has a specific rotation of $[\alpha]_D = +98{\cdot}36°$. Its *silver* salt, $AgC_{20}H_{29}O_3$, is obtained as a flocculent, white precipitate readily altered by light, the *methylic* salt crystallises in lustrous, white needles melting at 94—95°, and the *ethylic* salt in white needles melting at 79°. The acid does not combine with bromine in acetic acid solution.

β-trans-Camphandioic acid, $COOH{\cdot}C_9H_{15}{:}C_9H_{15}{\cdot}COOH$, is obtained in colourless, transparent, hemihedral, monosymmetric crystals melting at 265—266°; it has rather less than the normal molecular weight in freezing acetic acid, and in a 2·25 per cent. absolute alcohol solution at 18·5° has a specific rotation of $[\alpha]_D = +90{\cdot}6°$. The triacid *potassium* salt, $C_{20}H_{32}O_4,C_{20}H_{31}KO_4$, crystallises in microscopic prisms and is sparingly soluble in boiling water; the *silver* salt, $C_{20}H_{30}Ag_2O_4$, was also prepared. On heating the acid with acetic chloride at 120—130° for 2 hours, it yields *β-cis-camphandioic anhydride* $(C_{10}H_{15}O)_2O$ which is white and crystalline and melts at 162°; when treated with soda and then with hydrochloric acid, it gives *β-cis-camphandioic acid*, which crystallises in lustrous, white scales melting at 176—180° and has the normal molecular weight in freezing acetic acid.

α-Dicamphandioic anhydride, $\begin{matrix}C_9H_{15}{\cdot}CO \\ | \\ C_9H_{15}{\cdot}CO\end{matrix}\!\!>\!O$, crystallises in lustrous, white scales melting at 143—144°, gives the normal molecular weight in benzene and acetic acid by the cryoscopic method, and has a specific rotation of $[\alpha]_D = -142°$ in a 1·1 per cent. alcoholic solution at 14°. It separates unchanged on acidifying its solution in alkalis. The *silver* salt, $C_{20}H_{30}Ag_2O_4,H_2O$, of the corresponding acid was prepared.

W. J. P.

Coronilla and Coronillin. By C. FREDERIC SCHLAGDENHAUFFEN and E. REEB (*Chem. Centr.*, 1896, ii, 430—431; from *Zeit. Österr. Apoth.-V.*, **34**, 487—490, 507—510, 527—532).—The authors have examined the seeds of *Coronilla scorpioides* botanically and chemically. From the powdered seeds, about 4·3 per cent. of an orange-yellow, fatty oil of sp. gr. 0·912, was extracted by means of light petroleum. This oil, which becomes brown by the action of sulphuric acid and with ferric chloride turns violet, contains cholesterol and lecithin and on saponification yields oleic, arachic, stearic, and palmitic acids.

Coronillin is obtained by digesting the powdered seed, deprived of oil, with six times its weight of water at 100°, then adding an equal quantity of 95 per cent. alcohol, and after three days filtering and evaporating to one-sixth its weight. In about 24 hours, crystals of *pseudocoumarin*, $C_7H_4O_2$, separate, which on heating emit a coumarin-like odour. The filtrate from the crystals is evaporated to the consistency of the extract, the filtrate treated with 95 per cent. alcohol (for 50 grams extract 3 litres alcohol), the solution filtered, the alcohol distilled off, and the residue dissolved in water and shaken with ether. When the aqueous solution, after adding sodium sulphate and magnesium sulphate, is evaporated to 100 grams on the water bath, a thick mass separates; this is dissolved in alcohol, filtered, the filtrate treated with lead acetate, and the lead removed by hydrogen sulphide, the filtrate from this being evaporated to dryness, again dissolved in water, filtered through porcelain and again evaporated. The residue, after washing with boiling chloroform and ether and dissolving in a little alcohol, is finally treated with ether and the yellowish filtrate evaporated. The amber-coloured residue of coronillin is easily soluble in water, alcohol, and acetone, but only very slightly in ether and chloroform. It is a glucoside and is easily decomposed by dilute acids: $2C_7H_{12}O_5 + 3H_2O = C_8H_{18}O_7 + C_6H_{12}O_6$. With sulphuric acid, with sulphuric acid and bromine, with ferric chloride, and with potassium iodide, it gives very nearly the same reactions as the commercial brands of digitalin, although it does not give the blue reaction with Lafont's reagent. It is distinguished by the characteristic cherry red to reddish-brown coloration produced on the addition of nitric acid and a trace of cupric chloride. Its physiological action is very similar to that of the digitalis glucosides. E. W. W.

Rutin. By FRITZ WISCHO (*Chem. Centr.*, 1896, ii, 591; from *Pharm. Post.*, **29**, 333).—Rutin, which is obtained from rue, and quercitrin are isomeric compounds of a composition represented by Herzig's formula for the latter, $C_{36}H_{38}O_{20} + 3H_2O$. The product obtained by the decomposition of rutin with dilute mineral acids is named *isoquercetin*, and differs in physical properties from quercetin, which is similarly prepared from quercitrin. Isoquercetin is less soluble than quercetin, gives a dirty green coloration with ferric chloride which on warming turns bright red, whilst quercetin with ferric chloride forms a dark green solution which on warming becomes dark red. E. W. W.

Folia Bucco. By M. BIALOBRZESKI (*Chem. Centr.*, 1896, ii, 551—552; from *Pharm. Zeits. Russ.*, **35**, 353—358, 385—389, 401—405, 417—421,

433—436, 449—451).—The light petroleum extracts of *Folia Bucco longa* from *Barosma serratifolia* and of *Folia Bucco rotunda* from *B. betulina*, contain an ethereal oil besides some chlorophyll and resin. The oil, of which 1·88 per cent. is obtained from the former and 0·84 per cent. from the latter, is prepared by fractionating the acid petroleum extract under 14 mm. pressure to 130° and then distilling with steam. The resinous substance begins to boil at above 190° and has a brownish-green colour, an aromatic odour, and a bitter taste. After extraction with petroleum, the leaves, on treatment with cold alcohol, yield 3 per cent. of a brownish-green, bitter resin, insoluble in benzene and light petroleum. From the alcoholic extract of *B. serratifolia*, diosmin is deposited on the addition of sodium carbonate. Finally, by using hot 80—85 per cent. alcohol, a green acid extract is obtained which, on adding sodium carbonate, forms a precipitate of the sodium compound of diosmin, calcium carbonate, and manganese carbonate, from which diosmin is separated by treatment with 80—85 per cent. alcohol, washing with water containing 0·5 per cent. glacial acetic acid, and crystallising from hot alcohol. *B. betulina* yields 0·02 per cent. and *B. serratifolia* 0 045 per cent. of diosmin. This compound can also be obtained by washing the leaves with alcohol to which 0·2 per cent. of glacial acetic acid has been added.

The ethereal oil, which has a camphor and peppermint-like odour, boils at 178—235°, is very soluble in ether, alcohol, and benzene, and forms a green solution with ferric chloride. In the cold, it solidifies with separation of diosphenol—a phenol aldehyde which reduces oxide of silver and constitutes about 50 per cent. of the whole oil. Diosphenol may also be obtained by shaking the oil with potassium hydroxide solution. In order to free the liquid portion of the ethereal oil from diosphenol, it is fractionated under 15 mm. pressure and the portion boiling at 120—125°, which solidifies and consists mostly of the phenol, is pressed between filter paper. All the liquid fractions are freed from diosphenol by repeatedly shaking with silver oxide until the oil obtained by distilling with steam after adding sodium carbonate gives no coloration with ferric chloride. The diosphenol is thus converted into the sodium salt of *diosphenolic acid*, $OH\cdot C_6H_{14}\cdot COOH$, and is obtained as a white, amorphous, deliquescent powder insoluble in ether on treating the aqueous solution with animal charcoal, extracting with aqueous alcohol the white residue left on evaporation, again evaporating the solution, and drying in a vacuum. It can be further purified by washing with ether. Hydrochloric acid precipitates the acid from the sodium salt as a brown oil which may be purified to an almost colourless oil by converting it into the sodium salt and purifying this as above described. On fractionation under 14 mm. pressure, the liquid ethereal oil free from diosphenol yields a small distillate boiling at 64—67°, and a larger one boiling at 96—99°. After drying with potassium carbonate, these fractions boil respectively at 174—176° and 206—209° under the ordinary pressure.

Diosphenol, $OH\cdot C_6H_{14}\cdot CHO$, on crystallisation from alcohol, forms lustrous, colourless crystals having an odour like that of camphor, melts at 82°, and boils at 232° under the ordinary pressure and at 112° under 14 mm. pressure. The *oxime* melts at 156°. The phenyl-

hydrazine compound forms a blood-red liquid which solidifies at 0°, but was not obtained pure. On reduction with sodium in an aqueous ethereal solution, diosphenol yields the *alcohol* $C_6H_{14}(OH)\cdot CH_2\cdot OH$, which melts at 159°.

By heating with alcoholic potash, diosphenol forms an *acid* which melts at 97°, and whose composition differs from that of diosphenolic acid by containing one more molecule of water.

The fraction of the oil boiling at 206—209° is a *ketone*, $C_{10}H_{18}O$, isomeric with menthone; it has a peppermint-like odour, and decolorises potassium permanganate solution. Its sp. gr. $= 0.8994$ at 18·5°, its specific rotatory power $[\alpha]_D = -6.12°$. The *oxime* is a faintly green liquid of sp. gr. 0·9627 at 18·5°, boils at 134—135°, and has a specific rotatory power $[\alpha]_D = +2.19°$. The bromine derivative, $C_{10}H_{17}OBr_3$, is a brown, fuming liquid.

The fraction of the oil which boils at 174—176° corresponds with terpene in composition, has a sp. gr. $= 0.8647$ at 18·5°, a specific rotatory power $[\alpha]_D = +60.40°$, and decolorises potassium permanganate and bromine.

Diosmin forms minute, tasteless, and odourless white or yellow needles, is soluble in hot alcohol, melts at 244°, and by the action of dilute sulphuric acid yields a carbohydrate and an uninvestigated substance which melts at 197°.
E. W. W.

Pharmacology of Kola. By P. CARLES (*Chem. Centr.*, 1896, ii, 552—553; from *J. Pharm.*, [vi], 4, 104—108).—The valuation of kola nuts is best carried out by extraction with chloroform containing alcohol. Ten grams of the fine powder are mixed with 1 gram of calcium hydroxide and 20 grams of 80 per cent. alcohol, and dried until the weight is about 13·5 to 14 grams. The mass is then boiled for an hour with a mixture of 100 grams of chloroform and 20 grams of 90 per cent. alcohol, and this operation repeated three times. The alcohol keeps the powder in a fixed condition of hydration, dissolves the kolanine, ensures its decomposition by the lime, and prevents spirting of the liquid during evaporation. There are many substances found in plants which are analogous to Heckel's kola-red or Knebel's kolanine, which the author regards as a compound of kola-tannic acid with the kola alkaloids. If fresh, ripe, undamaged kola nuts are immersed in alcohol, they do not perceptibly colour it, hence, according to the author, the nuts contain little kolanine, which is only formed under the influence of air, light, warmth, and moisture. This oxidation, which is dependent on the action of the enzyme laccase, takes place extremely quickly, for a freshly cut surface of a broken nut becomes green instantly when moistened with tincture of guaiacum. Kolanine is very similar to cachou, and is always mixed with resin and other substances. Dried Congo nuts contain kolanine in a quantity equivalent to 20 per cent. of caffeine, the Indian nuts 16 per cent., and Dahomey nuts 20 per cent. The best solvent for kolanine is 70 per cent. alcohol. It is insoluble in chloroform, slightly soluble in water, but very easily soluble in dilute alkalis with decomposition. Lime and the alkaline earths decompose it, without dissolving it, in presence of water or boiling alcohol, hence the use of an alkali in the evaluation of

the nuts. Aqueous acids decompose kolanine with production of very pure caffeine, but the author was unable to detect glucose, which Knebel and Heckel state also to be a product of the decomposition. Caffeine and theobromine constitute about one-fifth of the weight of kolanine.

The amount of kolanine in the nut or the extract is determined by extracting with cold water, then with 70 per cent. alcohol, washing the product with cold water, and drying at 100°. To estimate the alkaloids, a mixture of 1 gram with 1 gram of lime, 3 grams of chalk, and 6 grams of 70 per cent. alcohol is extracted with alcohol and chloroform. E. W. W.

Compounds from Lichens. By WILHELM ZOPF (*Annalen*, 1897, **295**, 257—300. Compare this vol., i, 362).—*Lecanora atra* (Acharius), obtained in Sicily, has been shown by Paternò to contain usnic and atralinic acids, whilst specimens collected in Italy yield usnic and atranoric acids. The author finds that the lichen derived from more northerly sources contains atranoric acid along with *lecanorol*, $C_{27}H_{30}O_9,H_2O$, identical with the substance obtained by Paternò and Crosa from *Lecanora sulphurea* (Abstr. 1894, i, 541); these two compounds are also present in *Lecanora grumosa* (Persoon). *Lecanora cenisea* (Ach.), however, contains atranoric and roccellic acids, the latter, which has the formula $C_{17}H_{32}O_4$, being the acid isolated by Schunck and by Hesse from *Roccella tinctoria*. *Lecanora sordida* (Pers.), collected in the neighbourhood of Halle, contains atranoric and zeoric acids, and it is therefore probable that the variety from an Italian source, examined by Paternò and found to contain zeorin, sordidin, and usnic acid, was not the same species. *Lecanora campestris* (Schaerer) contains atranoric acid, and *Lecanoria badia* (Pers.), stereocaulic acid; from *Lecanora varia* (Ehrh.) has been isolated psoromic acid, but no trace of atranoric acid.

Acolium tigillare (Ach.), which is identical with *Calicium tigillare* (Pers.) and with *Cyphelium tigillare* (Fries), contains rhizocarpic acid, and it is probable that this substance is also present in *A. viridulum.*

Parmelia saxatilis (L.), *var. sulcata* yields atranoric and stereocaulic acids, whilst *Parmelia tiliacea* (Hoffmann) contains atranoric and *parmelialic acid*, which crystallises in small needles, and melts, evolving gas, at 165°; the alcoholic solution of this substance develops a violet or purple-red coloration with ferric chloride, and bleaching powder gives rise to a beautiful red colour, thus affording a distinction from evernic acid, which in some respects it resembles. Parmelialic acid dissolves in alkali carbonates, liberating carbonic anhydride, and yields orcin when treated with hot, dilute caustic potash; it dissolves freely in alcohol, sparingly in chloroform, and scarcely at all in light petroleum. *Parmelia perlata* (Ach.) contains atranoric and hæmatommic acids, and not parmelin and vulpic acid, as stated by Hesse (Abstr., 1895, i, 299).

Parmelialic acid has been also obtained from *Urceolaria cretacea* (Massalongo), along with zeorin and atranoric acid; the latter substance occurs in *Parmelia aleurites* (Ach.), *Lecanora effusa* (Pers.), and *L. subfusca* (L.), being associated in the first named with stereocaulic acid,

and in *L. effusa* with usnic acid. Atranoric acid is found in *Evernia furfuracea* (L.), which does not contain a trace of usnic acid as stated by Rochleder and Heldt.

Parmelia physodes (L.) is described by Gerding as yielding physodin, which melts at 125°, whilst Hesse has obtained from this lichen ceratophyllin, melting at 147°; the author is unable to confirm these statements, having obtained only atranoric acid along with two compounds, one of which melts at 188—190°, whilst the other becomes reddish-brown above 200°, and chars completely at 260°. *Dimelaena oreina* (Ach.) contains zeorin and usnic acid.

Leprarin occurs to the extent of 5 per cent. in *Lepraria latebrarum* (Ach.), and crystallises from absolute alcohol in microscopic, lustrous leaflets melting at 155°; it is insoluble in water, and but sparingly soluble in alcohol, ether, chloroform, and benzene. The alcoholic solution develops a purple red coloration with ferric chloride, but the substance is indifferent towards bleaching powder; it dissolves in concentrated sulphuric acid without undergoing change. Roccellic acid is associated with leprarin in *L. latebrarum.*

A useful summary of the author's results brings the paper to a conclusion. M. O. F.

A Reply [Tetrahydropyridine Derivatives, &c.]. By ALBERT LADENBURG (*Annalen,* 1897, **295**, 370—374. Compare Lipp, this vol., i, 229).—A polemical paper, in which Lipp's conclusions (*loc. cit.*) regarding the accuracy of the author's results are emphatically challenged. It is claimed that 1-methylpipecolylalkine does exhibit isomerism, which may be explained on the hypothesis of asymmetric nitrogen. M. O. F.

Synthesis of Piperidine, and its β-Alkylated Homologues. By J. DARNELL GRANGER (*Ber.*, 1897, **30**, 1054—1059).—In Gabriel's process for the synthesis of piperidine, the greatest loss occurs when the γ-phenoxyvaleric acid is converted into the nitrile by means of lead thiocyanate; to avoid this, the author starts with ethylic cyanoacetate which on condensation with ethylic sodiomalonate yields *ethylic α-cyano-δ-phenoxyvalerate,* $OPh\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH(CN)\cdot COOEt$, a brown oil decomposing when distilled under diminished pressure. The *acid,* which melts at 62—67°, is extremely soluble, and cannot be recrystallised; at 200°, it loses carbonic anhydride, and yields an oil identical with Gabriel's δ-phenoxyvaleronitrile and giving ε-phenoxyamylamine on reduction.

No advantage is gained by using chloromethoxypropane instead of phenylic chloropropylic ether in this reaction, the *ethylic α-cyano-δ-methoxyvalerate* formed on condensing this substance with ethylic sodiomalonate being also decomposed during distillation. *Ethylic γ-methoxypropylmalonate* is a colourless oil boiling at 254—258°. J. F. T.

Resolution of Synthetic β-Propylpiperidine into its Active Constituents. By J. DARNELL GRANGER (*Ber.*, 1897, **30**, 1060—1065. Compare preceding abstract).—*β-Propylpiperidine,* prepared by treating β-propylchloramylamine with potash, is a clear, colourless liquid, which boils at 174° (758 mm.), and has a sp. gr. = 0·8475 at 26°. The

hydrochloride crystallises in long, colourless needles or prisms melting at 127—129°, and the *aurochloride* in lemon-yellow needles, melting at 95—98° after recrystallisation from water. With phenylthiocarbimide it yields *phenyl-β-propylpiperidinethiocarbamide*, $C_8H_{16}N\cdot CS\cdot NHPh$, which forms stellate groups of needles melting at 90·5°.

The resolution of β-propylpiperidine into its active constituents is effected by Marckwald's method, that is through the tartrates, *l-β-propylpiperidine d-tartrate* is obtained in large white prisms melting at 161°, when a solution of *d*-tartaric acid is added to β-propylpiperidine, and crystallisation started by the addition of a crystal of coniine tartrate. The base *l-β-propylpiperidine*, obtained from this tartrate by treatment with potash, boils at 174° (752·5 mm.), and has a rotation $\alpha_D = -5° 44'$, the *hydrochloride* melts at 147°.

d-β-Propylpiperidine l-tartrate, prepared in the same way, crystallises in long prisms melting sharply at 158°, and yielding, on treatment with potash, *d-β-propylpiperidine*, a substance showing the rotation $\alpha_D = 5° 55'$; its *hydrochloride* melts at 147°. J. F. T.

Indolinones. II. By KARL BRUNNER (*Monatsh.*, 1897, **18**, 95—122. Compare this vol., i, 100).—*3′ : 3′-Dimethyl-2′-indolinone*, $C_6H_4<{CMe_2 \atop NH}>CO$, was prepared by heating isobutyrylphenylhydrazide with three times its weight of quicklime for 2 hours at 170—200°, boiling the product for an hour with excess of hydrochloric acid in a reflux apparatus, and filtering off the indolinone. It crystallises in rhombic prisms of two different habits [$a:b:c = 0·8496:1:0·7219$], which were examined exhaustively from the crystallographical point of view; it melts at 151°, and boils at 302·5° under 759 mm. pressure. It forms no crystalline salts with acids but it gives a *silver* derivative,

$$C_{10}H_{10}AgNO,$$

which, when heated at 60° with methylic iodide in ethereal solution, yields a *lactime-ether*, $C_6H_4<{CMe_2 \atop \rule{1em}{0.4pt} N}\geqslant C\cdot OMe$, melting at 62°; and when heated with methylic iodide and sodium methoxide for 16 hours at 100—120°, it yields a lactam-ether, $C_6H_4<{CMe_2 \atop NMe}>CO$, (1′ : 3′ : 3′-trimethyl-2-indolinone), which has already been prepared. When boiled with acetic anhydride, it yields an *acetyl* derivative,

$$C_{10}H_{10}AcNO,$$

melting at 105°; with sodium nitrite, in cooled acetic acid solution, it yields a yellowish *nitroso*-derivative, $NO\cdot C_{10}H_{10}NO$, melting and decomposing at 60°; with nitric acid in acetic acid solution, it yields a yellowish-red *nitro*-derivative, $NO_2\cdot C_{10}H_{10}NO$, melting at 258° (together with a small quantity of another nitro-product which is yellow and melts at 186°); and in acetic acid solution it yields, with bromine water, a *dibromo*-derivative, $C_{10}H_9Br_2NO$, identical with the compound obtained from the trimolecular base $(C_{10}H_{11}N)_3$ (Abstr., 1896, i, 169).

3′ : 3′-Dimethyl-2′-indolinone can be reduced with sodium in boiling amyl-alcoholic solution to *3′ : 3′-dimethylindoline*, $C_6H_4<{CMe_2 \atop NH}>CH_2$, which is more conveniently prepared by reducing in the same manner

the above-mentioned trimolecular base. This indoline melts at 34—35°, and boils at 226—228° under 743 mm. pressure; it is best isolated by means of the sparingly soluble compound which it yields with potassium ferrocyanide. The *hydrochloride* turns yellow at 100° and melts at 172°; the reddish *platinochloride* melts and decomposes at about 200°; the *oxalate*, $C_{10}NH_{13},C_2H_2O_4$, melts at 139°. With nitrous acid, it yields a yellowish *nitroso*-derivative, $NO\cdot C_{10}NH_{12}$, which melts at 66°, and also, in the presence of excess of nitrous acid, a second compound, also yellowish, that melts at 192°, and is probably a *nitro-nitroso*-derivative, for it is formed by the action of strong nitric acid on the nitroso-compound. The indoline is oxidised by many oxidising agents; bromine water converts it into the dibromo-3′ : 3′-dimethyl-2′-indolinone mentioned above. It represents the third possible dimethylindoline, the other two being already known (2′ : 2′, Paal and Laudenheimer, Abstr., 1893, i, 38; 2′ : 3′, Steche, Abstr., 1887, 588; 1888, 298); that of Ciamician and Piccinini (this vol., i, 102) may be identical with any one of these three. C. F. B.

Quinolinesulphonic Acids. By ADOLPH CLAUS (*J. pr. Chem.*, 1897, [ii], **55**, 225—237).—Quinoline-4-sulphonic acid differs from the 1-isomeride in that it can be brominated without at the same time losing the sulphonic group. This is effected by dissolving it in strong hydrobromic acid, and adding a solution of bromine in acetic acid; the product is identical with the 3′-bromoquinoline-4-sulphonic acid of Claus and Schmeisser (Abstr., 1890, 266; apparently described there as 4′ : 4-bromoquinolinesulphonic acid). If the acid is brominated in the absence of water, the bromine being used either alone or in chloroform solution, the sulphonic group is lost, and a mixture of derivatives is obtained, as in the case of the 1-isomeride; the 4-sulphonic acid appears to yield 1 : 4 : 3′, the 1-isomeride 1 : 3 : 3′-tribromoquinoline, melting at 168·5° and 169—170° respectively, whilst both yield 1 : 3 : 4 : 3′-tetrabromoquinoline, melting at 205°. It is difficult to isolate and identify these products, for when obtained with constant melting point, they are found to be still impure.

Tetrahydroquinoline-4-sulphonic acid, $C_9NH_{10}\cdot SO_3H + H_2O$ (Lellmann, Abstr., 1888, 297), yields *ammonium*, with H_2O; *potassium*, with $\frac{1}{2}H_2O$; *barium*, with $3\frac{1}{2}H_2O$; *calcium*, with $2\frac{1}{2}H_2O$; *copper*, with $3H_2O$; *nickel*, with $3\frac{1}{2}H_2O$; *lead*, with $2\frac{1}{2}H_2O$; and anhydrous *silver* salts. When brominated, either with bromine alone, or in acetic acid or chloroform solution, the acid yields amongst other products 2-*bromo-tetrahydroquinoline*-4-*sulphonic acid*; this melts at 285°, and when brominated in aqueous solution with excess of bromine, appears to yield 3 : 4 : 3′-*tribromoquinoline* melting at 148°, together with other products. C. F. B.

Carbazole Derivatives. By EMIL VOTOČEK (*Chem. Centr.*, 1896, ii, 490; from *Rozpravy české akad.*, 1896, **5**, Kl. ii, Nr. 22).—Carbazole, when nitrated in glacial acetic acid at 80° with nitric acid of sp. gr. 1·38 (1 Mol.), yields *mononitrocarbazole*, which forms yellow flakes or needles melting at 210°. When Witt's method of nitration is employed, dinitro-derivatives are not obtained, as in the case of diphenylamine, but two mononitrocarbazoles are formed, the one, brown crystals melt-

ing at 210°, the other, lemon-yellow needles melting at 184°. By the action of a mixture of nitric acid (sp. gr. 1·4) with alcohol and glacial acetic acid on nitrosocarbazole, a dinitro-derivative is obtained which does not melt below 306°. The *diamidocarbazole* prepared from this crystallises in grey, silvery scales, decomposes above 260°, is slightly soluble in benzene, toluene, xylene, and alcohol, and its salts show a strong lignin reaction.

On treatment with excess of bromine, carbazole forms *tetrabromocarbazole,* which melts at 220°, and on boiling with nitric acid of sp. gr. 1·4 is converted into *tetrabromodinitrocarbazole,* which melts at 294°. By heating with carbon tetrachloride at 220°, a blue dye of the triphenylmethane type is formed by condensation. The condensation products with formaldehyde and benzaldehyde were not obtained in a crystalline form. In presence of concentrated sulphuric acid, carbazole gives, with benzaldehyde, a carmine red solution, which on pouring into water turns blue, with paranitrobenzaldehyde a ruby to magenta red coloration, with metanitrobenzaldehyde a dark red solution which turns green on addition of water, with vanillin a crimson red solution turning violet on dilution, with furfuraldehyde a carmine red to violet, and with glucose a violet coloration. A drop of concentrated sulphuric acid added to a hot solution of carbazole in acetic acid produces a violet coloration, and with a solution of carbazole and glucose a strong blue coloration. E. W. W.

The Pyrazole Series. By LUDWIG CLAISEN (*Annalen,* 1897, **295**, 301—324. Compare Abstr., 1894, i, 345).—The author has already shown that phenylhydrazine undergoes condensation with ethylic ethoxymethylenemalonate, yielding a phenylhydrazide, which is converted at 170° into ethylic 1 : 5 : 4-phenylpyrazolonecarboxylate (Abstr., 1895, i, 193); the present investigation deals with the action of phenylhydrazine on ethylic ethoxymethyleneacetate, and ethoxymethyleneacetylacetone.

[With C. NIEGEMANN and F. THOMAS.]—When phenylhydrazine and ethylic ethoxymethyleneacetate are mixed in ethereal solution at − 10°, the *phenylhydrazide,* $C_6H_8O_3$:CH·NH·NHPh, or $C_6H_9O_3$·CH:N·NHPh, separates in aggregates of small, colourless needles, and melts at 87—88°; it loses the elements of water under the influence of glacial acetic acid and concentrated hydrochloric acid, the same effect being produced when the substance is heated on the water bath.

Ethylic 1 : 5-*phenylmethylpyrazole*-4-*carboxylate,*

$$\begin{matrix}\mathrm{NPh\cdot CMe} \\ | \\ \mathrm{N{=\!=}CH}\end{matrix}\!\!>\!\mathrm{CH\cdot COOEt},$$

the product of internal condensation of the foregoing compound, crystallises from light petroleum in large, transparent, tabular prisms, melting at 55—56°; the *acid* crystallises from boiling water in short prisms, and melts at 167—168°. The *silver* salt resists the action of light, and the *calcium* salt, crystallising in leaflets, contains $2H_2O$, which is removed at 150°; the *methylic* salt separates from methylic alcohol in colourless prisms, and melts at 71°. 1 : 5-*Phenylmethylpyrazole,* $C_{10}H_{10}N_2$, produced on distilling the carboxylic acid, boils at 260—261° under a pressure of 753 mm., and has a sp. gr.

= 1·085 at 15°; it is therefore identical with the base obtained by distilling 1:5-phenylmethylpyrazole-3-carboxylic acid (Abstr., 1894, i, 346).

1-*Phenylpyrazole*-4 : 5-*dicarboxylic acid*, $\begin{matrix}\text{NPh·C(COOH)}\\ \vert \qquad\qquad \\ \text{N}\!=\!=\!=\!=\!=\!=\text{CH}\end{matrix}\!\!>\!\text{C·COOH}$, is prepared by oxidising a boiling alkaline solution of phenylmethylpyrazolecarboxylic acid with potassium permanganate, and, after repeated crystallisation from hot water, melts at 215—216°; neither the acid nor its salts can be regarded as identical with the so-called 4 : 5-dicarboxylic acid of Balbiano and Severinini. The acid crystallises in short prisms, and yields a fluorescent compound with resorcinol and sulphuric acid; the *hydrogen barium* salt crystallises in small needles, and the *silver* salt is amorphous. The *methylic* salt crystallises from methylic alcohol in silky needles, melting at 75—76°, and is converted by ammonia into the *monamide* and *diamide* which crystallise in needles, and melt at 186° and 253—255°, respectively; the *dianilide* dissolves with difficulty in alcohol and ethylic acetate, and melts at 205—206°. Rapid distillation of the dicarboxylic acid converts it into 1 : 4-phenylpyrazolecarboxylic acid, which melts at 221—222°, 1-phenylpyrazole being produced when the dicarboxylic acid is boiled in a reflux apparatus.

4 : 1 : 5-*Acetylphenylmethylpyrazole*, $\begin{matrix}\text{NPh·CHMe}\\ \vert \qquad\qquad \\ \text{N}\!=\!=\!=\!=\text{CH}\end{matrix}\!\!>\!\text{C·COMe}$, obtained by the action of phenylhydrazine on ethoxymethyleneacetylacetone in ethereal solution, crystallises from light petroleum in colourless prisms; it melts at 107—108°, and boils at 331—333° (corr.), under a pressure of 745 mm. The *methiodide* crystallises in small, colourless prisms, and melts at 166°. The *ketonic acid*, $\begin{matrix}\text{NPh·CHMe}\\ \vert \qquad\qquad \\ \text{N}\!=\!=\!=\!=\text{CH}\end{matrix}\!\!>\!\text{C·CO·COOH}$, produced on oxidising the substance with potassium permanganate, crystallises from water in white needles melting at 166°; the *phenylhydrazone* melts at 207—208°, and the *silver* salt crystallises from hot water in lustrous needles. The *isonitrosoketone*, $\begin{matrix}\text{NPh·CHMe}\\ \vert \qquad\qquad \\ \text{N}\!=\!=\!=\!=\text{CH}\end{matrix}\!\!>\!\text{C·CO·CH:NOH}$, is obtained on treating the ethereal solution of the pyrazole derivative with sodium and amylic nitrite; it crystallises from ethylic acetate in colourless, silky needles, and melts at 192°. Caustic soda resolves the isonitroso-derivative into hydrogen cyanide and 1 : 5 : 4-phenylmethylpyrazolecarboxylic acid. M. O. F.

Derivatives of 1-Phenyl-3 : 5-pyrazolidone and 1-Paratolyl-3 : 5-pyrazolidone. By Th. Asher (*Ber.*, 1897, **30**, 1018—1024).—1-Phenyl-3 : 5-pyrazolidone (Michaelis and Burmeister, *Ber.*, **25**, 1502) readily condenses with anisaldehyde to form 1-*phenyl*-4-*methoxybenzylidene*-3 : 5-*pyrazolidone*, $\text{NPh}\!<\!\begin{matrix}\text{NH·CO}\\ \qquad\ \vert \\ \text{CO · C:CH·C}_6\text{H}_4\text{·OMe}\end{matrix}$, which crystallises in yellowish-red needles, and melts at 246°.

1-*Phenyl*-4-*cinnamylidene*-3 : 5-*pyrazolidone*,

$$\text{NPh}\!<\!\begin{matrix}\text{NH·O}\\ \qquad \vert \\ \text{CO · C:CH·CH:CHPh}\end{matrix},$$

is obtained in a similar manner from cinnamaldehyde and melts at 252°, whilst 4-*dibromophenylpyrazolidone*, obtained by the direct action of bromine, crystallises in golden yellow needles melting at 243°. When phenylpyrazolidone is boiled with chloroform, a *condensation product* of unknown constitution is formed which melts at 303°.

1-*Paratolyl*-3 : 5-*pyrazolidone*, $C_6H_4Me\cdot N<\begin{matrix}NH\cdot CO\\ CO\cdot CH_2\end{matrix}$, prepared by the hydrolysis of the product of the action of paratolylhydrazine on ethylic chloromalonate, crystallises in white plates melting at 204°; the *basic lead* salt, $C_{10}H_9N_2O_2\cdot Pb\cdot OH$, is a yellow precipitate. 1-*Paratolyl*-4-*benzylidene*-3 : 5-*pyrazolidone* melts at 253°; the corresponding acetone derivative, *paratolyl*-4-*isopropylidenepyrazolidone*, melts at 174°. *Tolyl*-4-*isonitrosopyrazolidone* crystallises in red needles melting at 182°, and is soluble in alkalis. 1-*Paratolyl*-3 : 5-*pyrazolidone*-4-*phenylhydrazone* is obtained by the action of diazobenzene chloride on the pyrazolidone, and crystallises in golden yellow plates melting at 234°.

2 : 4-*Dibenzoyl*-1-*paratolylpyrazolidone*, $C_6H_4Me\cdot N<\begin{matrix}NBz\cdot CO\\ CO-C:CPh\cdot OH\end{matrix}$, the constitution of which is not quite certain, crystallises in white plates melting at 133°. 1-*Paratolyl*-4-*dibromopyrazolidone* crystallises in prisms melting at 174°. Tolylpyrazolidone also appears to combine with a molecule of tolylhydrazine to form an additive *compound*, $C_{17}H_{20}N_4O_2$, which crystallises in white plates melting at 182°, and has basic properties.

Malonyl chloride reacts with phenylhydrazine to form malonyl dihydrazide, $CH_2(CONH\cdot NHPh)_2$, melting at 184°, and with paratolylhydrazine hydrochloride to form tolylpyrazolone in small quantity.

A. H.

Pyrazinetricarboxylic Acids and their Products of Decomposition. By CARL STOEHR and W. DETERT (*J. pr. Chem.*, 1897, [ii], 55, 248—262).—2 : 5-Dimethyl-3-ethylpyrazine, $N<\begin{matrix}CMe:CH\\ CEt\cdot CMe\end{matrix}>N$, (compare Abstr., 1893, i, 486), when oxidised with permanganate on the water bath, is to a large extent completely oxidised, but yields some *pyrazine*-2 : 3 : 5-*tricarboxylic acid*, $C_4N_2H(COOH)_3 + 2H_2O$. This melts at 164°, but when anhydrous, it melts and decomposes at 180°. The *silver*, $C_7HN_2O_6Ag_3 + H_2O$; *barium*, with $4H_2O$; *calcium*, with $12H_2O$; *strontium*, with $12H_2O$; and *cadmium*, with $9H_2O$ salts were prepared; with the exception of the silver salt, these retain some of their water of crystallisation at 160°.

The acid itself loses carbonic anhydride when boiled with water; after boiling for 2—3 days, the products are 2 : 5-pyrazinedicarboxylic acid (*loc. cit.*; also Wolff, *ibid.*, p. 373) and an isomeric acid. Of the first, the *potassium*, $C_4N_2H_2(COOK)_2$; *sodium*, and *strontium*, with $5H_2O$, salts were prepared. The second product, $C_4N_2H_2(COOH)_2 + 2H_2O$, is probably *pyrazine*-3 : 5-*dicarboxylic acid*, for it does not yield an anhydride when heated with acetic anhydride, as we should expect a 2 : 3-dicarboxylic acid—the only other isomeride possible—to do. The acid which melts and decomposes at 217—218°, crystallises in monoclinic prisms; $a:b:c = 1\cdot0529:1:?$; $\beta = 62°\ 43\frac{1}{2}'$. It is more soluble in

alcohol than the 2:5-acid, and its salts are rather more soluble; several of these were prepared, and the *silver* salt, $C_6H_2N_2O_4Ag_2 + H_2O$, which retains its water obstinately, was analysed. C. F. B.

Action of Diphenyltetrazochloride on Ethylic Acetoacetate. By EDGAR WEDEKIND (*Annalen*, 1897, **295**, 324—339).—It has been shown that diazobenzene chloride converts the sodium derivative of ethylic acetoacetate into ethylic benzeneazoacetoacetate, whilst the presence of 2 molecular proportions of the azo-compound along with excess of alkali, gives rise to ethylic formazylformate (Abstr., 1893, i, 84); the author has therefore studied the action of diazotised benzidine on the salt.

[With PAUL NISSEN.]—*Ethylic cycloformazylformate*,

$$COOEt\cdot C\begin{cases} N\cdot NH\cdot C_6H_4 \\ N{=}N\cdot C_6H_4 \end{cases},$$

is obtained by simultaneously adding diphenyltetrazochloride and ethylic acetoacetate (1 mol.) to aqueous caustic potash at 0°, and is purified by precipitation with light petroleum from a solution in chloroform; it is an amorphous, reddish-brown powder, which becomes dark at 180°, sinters at 200°, and melts at 280°. The solution in concentrated hydrochloric and sulphuric acids is intensely green.

The *ethylic* salt of dibutanonic acid diphenyldihydrazone (*ethylic diacetylglyoxylate diphenyldihydrazone*), $C_{12}H_8[NH\cdot N\colon C(COMe)\cdot COOEt]_2$, is produced when diphenyltetrazochloride acts on two molecular proportions of ethylic acetoacetate, and crystallises from alcohol in small, yellow needles melting at 197—198°; towards alkalis, its behaviour resembles that of ethylic benzeneazoacetoacetate, dissolving in the gently heated agent, precipitation occurring as the temperature rises. The solution in concentrated sulphuric acid is yellowish-brown, and becomes deep red when treated with ferric chloride; with diazobenzene chloride (2 mols.), the alkaline solution yields a reddish-brown *compound* which melts at 235—240°.

Ethylic cyclodiphenyltetrazoliumchloridecarboxylate,

$$COOEt\cdot C\begin{cases} N\cdot NCl\cdot C_6H_4 \\ N{=}N\cdot C_6H_4 \end{cases},$$

is obtained by oxidising ethylic cycloformazylformate with amylic nitrite and alcoholic hydrogen chloride, and sinters indefinitely at 206°; the alcoholic solution gives a yellow precipitate with picric acid or gold chloride, and concentrated sulphuric acid slowly produces a brownish-red solution. Reducing agents regenerate ethylic cycloformazylformate.

Bisphenylmethylpyrazoloneazodiphenyl, $C_{12}H_8\left(N\colon N\cdot CH\begin{cases} CO{-}NPh \\ CMe\colon N \end{cases}\right)_2$, obtained by heating the ethylic salt of dibutanonic acid diphenyldihydrazone with phenylhydrazine dissolved in glacial acetic acid, is a bright red, micro-crystalline powder, which melts and evolves gas at 289°; it dissolves with extraordinary difficulty in common solvents, and forms a deep red solution in concentrated hydrochloric acid. 1:3-Phenylmethylpyrazolone-4-azobenzene melts at 155°.

Diphenyltetrazochloride combines with malonic acid, yielding a red-

dish-brown *compound* which is insoluble in all media excepting concentrated sulphuric acid. M. O. F.

Derivatives of Ditriazole from Cyanophenylhydrazine and Cyanohydrazine. By ERICH L. RINMAN (*Ber.*, 1897, **30**, 1193—1195).—Dicyanophenylhydrazine has the constitution $NHPh \cdot N \colon C(CN) \cdot NH_2$, and when mixed with phenylhydrazine (1 mol.) and a very small quantity of alcohol, it yields cyanophenylhydrazine; the author therefore ascribes to the latter substance the formula $C_2(NH_2)_2(N \cdot NHPh)_2$.

When cyanohydrazine is treated with boiling formic acid in a reflux apparatus, *ditriazole*,

$$\begin{matrix} N\cdot NH \\ \| \\ CH\cdot N \end{matrix} \!>\! C\cdot C \!<\! \begin{matrix} NH\cdot N \\ \| \\ N\text{—}CH \end{matrix} \quad \text{or} \quad \begin{matrix} NH\cdot N \\ | \\ CH\colon N \end{matrix} \!>\! C \!<\! \begin{matrix} N\cdot NH \\ | \\ N\colon CH \end{matrix},$$

is produced; this crystallises from a mixture of glacial acetic acid and concentrated hydrochloric acid in colourless scales, and sublimes above 300° in prismatic crystals. M. O. F.

Derivatives of Isoxazolone. By ROBERT SCHIFF and G. VICIANI (*Ber.*, 1897, **30**, 1159—1166).—By eliminating alcohol from the oxime of derivatives o ethylic acetoacetate, a large number of compounds of the type $N \!<\! \begin{matrix} O\text{—}CO \\ \quad\;\; | \\ CMe\cdot CXY \end{matrix}$ can be prepared.

Methylchlorisoxazolone, $N \!<\! \begin{matrix} O\text{—}CO \\ \quad\;\; | \\ CMe\cdot CHCl \end{matrix}$, prepared from the oxime anilide of ethylic α-chloracetoacetate, melting at 112°, by treating it with sodium hydroxide solution; it separates from hot benzene in colourless crystals melting at 86—87°.

The oximeanilide of ethylic benzylacetoacetate, at the moment of its formation,passes into *methylbenzylisoxazolone*, $N \!<\! \begin{matrix} O\text{—}CO \\ \quad\;\; | \\ CMe\cdot CH\cdot C_7H_7 \end{matrix}$, which crystallises from dilute methylic alcohol in glistening prisms melting at 106°, and is acidic, forming two kinds of salts of the types

$$OH\cdot N\cdot CMe\cdot CH(C_7H_7)\cdot COOM$$

and $N \!<\! \begin{matrix} O\text{—}CO \\ \quad\;\; | \\ CMe\cdot C(C_7H_7)\cdot M \end{matrix}$ respectively, the salts of the alkali metals having the former, whilst those of the heavy metals have the latter constitution; the *phenylhydrazone* of *methylisoxazolone* melts and decomposes at 192°, the *orthanisylhydrazone* melts at 172—173°, the *orthotolylhydrazone* at 154—155°, the *paratolylhydrazone* at 202°, the *α-naphthylhydrazone* at 168—170°, the *β-naphthylhydrazone* at 200°, and the *paroxyphenylhydrazone* at 219—220°, with decomposition.

J. F. T.

Isoxazolones. By RUDOLF UHLENHUTH (*Annalen*, 1897, **296**, 33—62).—Phenylisoxazolone is prepared by Hantzsch's method (Abstr., 1891, 740), and, according to the author, melts at 152°; the *potassium* derivative crystallises in colourless, nacreous scales, the *barium* and *calcium* derivatives are anhydrous, whilst the *strontium* derivative contains $1H_2O$. The *silver* derivative is sensitive towards light, and the *cadmium* derivative contains $5H_2O$; the *copper*, *zinc*

and *lead* derivatives have been also prepared. The *methylamine* and *ethylamine* derivatives are crystalline, and melt at 95° and 108° respectively, the *dimethylamine* and *diethylamine* derivatives are oils, and decompose in the desiccator, whilst the *aniline* derivative crystallises in colourless, quadratic leaflets, and melts at 110—111°; the *toluidine* and *phenylhydrazine* derivatives melt and decompose at 117° and 153° respectively, and the piperidine derivative is an oil. The silver derivative of phenylisoxazolone acts on alkylic iodides, forming the *methyl* and *ethyl* derivatives, which melt at 78° and 76° respectively.

The preparation of methylisoxazolone is attended with some difficulties, but small quantities may be obtained by heating the oxime of ethylic acetoacetate with ammonia, and decomposing with hydrochloric acid the derivative of methylisoxazolone so produced; this substance, the properties of which have been described by Hantzsch, melts at 169—170°, and is bimolecular in naphthalene. The *potassium* derivative crystallises in colourless, monoclinic plates, and the *methylamine, ethylamine, dimethylamine,* and *diethylamine* derivatives are also crystalline, and melt at 177—178°, 135—136°, 109—111°, and 112—114° respectively; the *aniline, naphthylamine,* and *phenylhydrazine* derivatives melt at 150—151°, 116°, and 102—103° respectively. The *methyl* derivative crystallises in transparent, four-sided prisms, and melts at 74—75°; the *ethyl* derivative melts at 90—91°.

Dimethylisoxazolone, $\begin{matrix}\mathrm{N{:}CMe}\\ |\qquad\\ \mathrm{O{-}CO}\end{matrix}\!>\!\mathrm{CHMe}$, is obtained by agitating a concentrated solution of hydroxylamine hydrochloride to which the calculated amount of caustic soda has been added with ethylic methylacetoacetate, the liquid being cooled meanwhile by a freezing mixture; the ethereal salt is dissolved during the process, and concentrated hydrochloric acid is then added in sufficient quantity to liberate dimethylisoxazolone as a crystalline precipitate. It melts and decomposes at 123—124°, and dissolves readily in alkalis and alkali carbonates; ferric chloride develops a reddish-brown coloration with the alcoholic solution. The *ammonium* derivative crystallises in aggregates of concentric prisms, and loses ammonia in moist air; the *hydrogen barium* derivative crystallises in needles containing $5\frac{1}{2}H_2O$, and melts at 167—175°. The *silver* derivative melts and decomposes at 218°, and the *hydrogen silver* derivative resists the action of light, and melts at 197°.

Methylethylisoxazolone, $\begin{matrix}\mathrm{N{:}CMe}\\ |\qquad\\ \mathrm{O{-}CO}\end{matrix}\!>\!\mathrm{CHEt}$, is prepared from hydroxylamine and ethylic ethylacetoacetate in the same way as the foregoing substance; it crystallises in white needles or prisms, melts at 50°, and develops a reddish-brown coloration with ferric chloride. The *barium* derivative contains $5\frac{1}{2}H_2O$, which is lost at 110°, and the *hydrogen silver* derivative is crystalline, and melts at 154°. M. O. F.

Action of Hydroxylamine on Ethylic Dicarboxyglutaconate. By SIEGFRIED RUHEMANN (*Ber.*, 1897, **30**, 1083—1087).—When ethylic dicarboxyglutaconate is suspended in alcohol and treated with hydroxylamine hydrochloride, a reaction takes place, and *ethylic pyroxolone-*

carboxylate, $COOEt\cdot C\!\!<\!\!\begin{smallmatrix}CO\cdot NH\\ CH\cdot O\end{smallmatrix}$, is produced, which crystallises in colourless prisms, and melts and decomposes at 168°. It gives a deep red coloration with ferric chloride, and possesses well-marked acid properties. The *silver salt* crystallises in lustrous plates, and decomposes suddenly when heated. The *ammonium salt* crystallises in long needles. When boiled with aqueous potash, the ethylic salt is decomposed with formation of malonic acid, ammonia, carbonic anhydride, and alcohol. When the silver salt is heated with methylic iodide, *ethylic methylpyroxolonecarboxylate*, $COOEt\cdot C\!\!<\!\!\begin{smallmatrix}CO\cdot NMe\\ CH\cdot O\end{smallmatrix}$, is produced, which crystallises in colourless prisms, melting at 96—97°, gives no coloration with ferric chloride, does not yield metallic salts, and is decomposed by potash with formation of methylamine. This reaction proves that the original ethylic pyroxolonecarboxylate contains an imido-group.

The author proposes to give the name pyroxolone to the group $HC\!\!<\!\!\begin{smallmatrix}CO\cdot NH\\ CH\cdot O\end{smallmatrix}$, from which this substance is derived. A. H.

Derivatives of Amido-orcinol and of Methylamido-orcinol. By FRS. HENRICH (*Ber.*, 1897, **30**, 1104—1110. Compare this vol., i, 404).—Amido-orcinol, when warmed with benzoic chloride, yields *parabenzoyloxy-β-phenylorthotoluoxazole*, $COOPh\cdot\overset{\displaystyle CH{:}CMe\cdot C\cdot N}{C{=\!=}CH{-}C\cdot O}\!\!>\!\!CPh$; this crystallises from absolute alcohol in colourless, long, thin plates, melts at 133°, and is readily soluble in ether, benzene, chloroform, and ethylic acetate, also in hot alcohol or hot acetic acid. *Parahydroxy-β-phenylorthotoluoxazole*, obtained by the action of alcoholic potash on the above benzoyl derivative, crystallises in long plates, melts at 239—239·5°, and is only sparingly soluble in cold alcohol, benzene, or ether. When warmed with acetic anhydride, it yields an *acetyl* derivative melting at 113—114°, which is readily soluble in ether and benzene.

When amido-orcinol is warmed with acetic anhydride, the chief product is *triacetylamido-orcinol*, which crystallises from dilute alcohol in colourless plates. It melts at 98—99°, and is readily soluble in alcohol, benzene, acetone, and chloroform.

Diacetylmethylamido-orcinol is obtained by the action of anhydrous sodium acetate and acetic anhydride on methylamido-orcinol; it crystallises from dilute alcohol in large twinned plates, melts at 108—109°, and is extremely readily soluble in benzene, chloroform, and acetic acid. An alkaline solution of methylamido-orcinol is readily oxidised either by the air or by hydrogen peroxide to a compound, $C_{15}H_{14}O_3N_2$, which crystallises in dark red needles, and melts at 253°; the authors have proved that this compound contains only one methoxy-group. It is only sparingly soluble in alcohol, ether, or cold benzene, practically insoluble in light petroleum, but more readily soluble in warm benzene, acetic acid, or ethylic benzoate. It is soluble in concentrated sulphuric acid, yielding a deep red solution. Nitrous acid develops a deep blue colour, which slowly disappears.

This compound, and also those obtained by the oxidation of amido-orcinol, are being further investigated. J. J. S.

Derivatives of Phenopenthiazole. By HEINRICH KIPPENBERG (*Ber.*, 1897, **30**, 1141—1147).—Of the two methods for the preparation of μ-alkylphenopenthiazoles devised by Gabriel and Posner (Abstr., 1895, i, 191), that from orthamidobenzylic alcohol and the acid chloride or anhydride is the more suitable when the formation of fatty substituted compounds are desired; whilst the second method, namely, melting orthamidobenzylic chloride hydrochloride with thiamides, is best adapted for the preparation of aromatic derivatives. *μ-Paratolylphenopenthiazole* $C_6H_4<\begin{smallmatrix}CH_2\cdot S\\ N=C\cdot C_7H_7\end{smallmatrix}$, prepared by the latter method, crystallises from dilute alcohol in microscopic needles melting at 109—110°, and *μ-orthotolylphenopenthiazole* from amidobenzylicbromide hydrobromide, and orthotolylthiamide in pale yellow scales softening at 54·5—56°.

μ-Paramethoxyphenylphenopenthiazole, $C_6H_4<\begin{smallmatrix}CH_2\cdot S\\ N=C\cdot C_6H_4\cdot OMe\end{smallmatrix}$, from the hydrochloride of amidobenzylic chloride and anisthiamide, melts at 124·5° after recrystallisation from dilute alcohol; it gives neither a platinum nor a gold salt.

μ-Ethylphenopenthiazole, $C_6H_4<\begin{smallmatrix}CH_2\cdot S\\ N=CEt\end{smallmatrix}$, can be prepared from thiopropionamide and orthamidobenzylicbromide hydrobromide, but is best obtained from amidobenzylic alcohol and propionic anhydride, subsequently treating the product with phosphorous pentasulphide; it boils at 270—272° (758 mm.), and yields a *hydrobromide* melting at 180—181°, a *picrate* which crystallises from alcohol in yellowish-red prisms melting at 135—136°, and also a *platinochloride*. In the formation of μ-ethylphenopenthiazole, a crystalline compound is also produced which separates from absolute alcohol in clusters of glistening needles melting at 190—191°; it is evidently *orthopropionylamidobenzylic bisulphide*, $C_{20}H_{24}O_2N_2S_2$, since it is identical with the compound produced from orthamidobenzylic bisulphide and propionic anhydride. *μ-Propylphenopenthiazole*, prepared from orthamidobenzylic alcohol and butyric anhydride in the usual way, boils at 282—284° (27 mm.) and yields a *picrate* crystallising from hot alcohol in yellow needles melting at 142—145°. J. F. T.

Action of Tannin and Gallic Acid on some Alkaloids. By WILLIAM OECHSNER DE CONINCK (*Compt. rend.*, 1897, **124**, 773—776).—An aqueous solution of tannin immediately precipitates pure and anhydrous nicotine, and an alcoholic solution precipitates nicotine from its solution in alcohol. Ethereal solutions behave in the same way. Gallic acid has no action on pure nicotine, but in presence of water a deep orange-red coloration is developed more rapidly than with tannin.

With cicutine or its aqueous solutions, neither dry tannin nor dry gallic acid produces any reaction, but with the aqueous solutions a blood-red colour soon develops. An aqueous solution of tannin precipitates pure and anhydrous cicutine, and alcoholic or ethereal solutions precipitate the corresponding solutions of the alkaloid. The reactions

are somewhat sensitive, but nicotine is precipitated by tannin from much more dilute solutions than cicutine. C. H. B.

Alums of Nitrogenous Bases. By N. A. ORLOFF (*Chem. Centr.*, 1896, ii, 590—591; from *Pharm. Zeit. Russ.*, **35**, 465—468, 481—484, 497—498).—The author has confirmed the general applicability of Kirschmann's method of forming alkaloid alums. A solution containing the sulphates of the alkaloid and of aluminium or chromium was evaporated at 50° to a small volume and allowed to crystallise in a cool place. If an alum has been formed, octahedral crystals separate on adding a crystal of potash alum. Solutions which do not yield alums on further concentration deposit aluminium sulphate and eventually the sulphate of the alkaloid. Alums of *piperidine, coniine, cocaine, atropine, quinine* and *sparteine* were prepared, whilst pyridine, pilocarpine, berberine, morphine, codeine, and chelerythrine did not yield alums. Thus the alkaloids derived from hydropyridine form alums, but the pyridine derivatives are incapable of doing so. Carbamide does not form an alum, but *allylcyanamide* prepared from thiosinamine by the action of oxide of lead or of oxide of mercury, forms an easily crystallisable alum when it is dissolved in dilute sulphuric acid, mixed with aluminium sulphate, evaporated at 30—40° to a syrup, and allowed to stand twelve hours.

Asparagine alum, $(C_4H_8N_2O_3)_2,H_2SO_4,Al_2(SO_4)_3 + 24H_2O$, forms octahedral crystals. E. W. W.

Cuskhygrine Hydrate. By CARL T. LIEBERMANN and FRITZ GIESEL (*Ber.*, 1897, **30**, 1113—1115. Compare Abstr., 1895, i, 310). —*Cuskhygrine hydrate*, $C_{13}H_{24}N_2O + 3\frac{1}{2}H_2O$, is obtained from a moist ethereal solution of the base, but if the solution is dried with potassium carbonate, the oily base itself is formed. It crystallises in colourless needles, melts at 40—41°, and has the same solubilities as cuskhygrine itself. The hydrate may easily be obtained as a hard, crystalline mass by adding 21·4 per cent. of water to the base. It begins to lose its water on exposure to the air, more readily when placed over potash, or when heated. The hydrate is capable of absorbing carbonic anhydride, yielding an unstable carbonate.

J. J. S.

Argine and Arginine. By ANASTASIO QUIROGA (*Bull. Soc. Chim.*, 1897, [iii], **15**, 787—791).—The author uses the name arginine for an alkaloid obtained from a tree which he terms argine, one of a class called by the natives of Paraguay *virarô-mi*. The alkaloid forms prismatic crystals, is not altered in air or on exposure to light, and is soluble in alcohol, chloroform, or benzene, but only sparingly so in ether, light petroleum, or water. Its reaction with the ordinary alkaloidal reagents are described. M. W. T.

NOTE.—This new alkaloid would be better named *argine*, the name "arginine" being already applied to a well-known base.—EDITORS.

Organic Chemistry.

American Petroleum. By CHARLES F. MABERY and ARTHUR S. KITTELBERGER (*Amer. Chem. J.*, 1897, **19**, 374—381).—A sample of petroleum, collected near the Magdalena River in the United States of Colombia, S. America, was found to consist practically of a single series of hydrocarbons, very possibly C_nH_{2n}; not more than a trace of aromatic hydrocarbons was present. The crude oil was dark in colour, thick, and viscous; it had sp. gr. = 0·9480 at 20°, absorbed bromine equivalent to 12·09 per cent., and contained ash 0·011, sulphur 0·68, nitrogen 0·318, carbon 85·63, and hydrogen 11·90 per cent.

A sample of petroleum from Oregon also contained but a trace of aromatic hydrocarbons, and had a composition intermediate between those required by the series C_nH_{2n+2} and C_nH_{2n-6}. The crude oil was thick and dark, had sp. gr. = 0·9597 at 20°, and contained sulphur 1·19, nitrogen 0·868, carbon 86·06, and hydrogen 11·87 per cent.

C. F. B.

Constituents of Petroleum between 150° and 220°. By CHARLES F. MABERY (*Amer. Chem. J.*, 1897, **19**, 419—482).—On account of the conflicting statements and erroneous assumptions concerning the composition of Pennsylvanian petroleum boiling above 150°, based on Markownikoff's results on Russian oil, the author has further studied this, as well as Ohio and Canadian petroleums. The two principal objects in view were (*a*) to determine the nature of the series of hydrocarbons which form the main body of American petroleum, and (*b*) to ascertain whether the composition of Pennsylvanian, Ohio, and Canadian petroleums is, as regards their principal constituents, the same.

Generally speaking, the separation of the constituents with higher boiling point presents greater difficulties than of those in the portions boiling below 150°. In the latter case, there is no danger of decomposition, which is, however, met with in the former, on account of the presence of unstable substances such as nitrogen, oxygen, and sulphur compounds. The difficulty may be overcome by distillation in a vacuum, but the hydrocarbons separated in this manner may before purification be contaminated by other substances whose boiling points are nearly the same.

As it was found that cracking in refining does not begin to any considerable extent below 225°, refinery distillates were generally used, especially from Pennsylvanian oil. Most of the results on Ohio and Canadian oils were obtained from vacuum distillates, the preparation of which has been previously described (*Amer. Chem. J.*, **17**, 713).

Pennsylvanian Petroleum.—As a result of this examination, it may be stated that the constituents with boiling points 163—164°,

173—174°, 196—197°, and 215—216° constitute the main body of this petroleum within these limits, and that they are members of the hydrocarbon series C_nH_{2n+2}. Any other substances present are found only in comparatively small quantities. No direct estimation can be based on these observations as to the proportion of aromatic hydrocarbons present, but among those identified may be mentioned mesitylene, cumene, pseudocumene, cymene, isocymene, durene, and isodurene.

For the separation of the hydrocarbons, refinery distillate at 48—50° Baumé, specific gravity 0·7892 at 20°, was used. It was nearly colourless, and gave no odour of decomposition.

Decane, $C_{10}H_{22}$, 163—164°.—The fraction of the crude oil 150—170° was carried through a long series of distillations until a large amount collected between 158—162° at 730 mm., and finally 162—163° at 760 mm. A portion of the oil, after being dried over sodium, being still impure, was purified by treatment with a mixture of nitric and sulphuric acids, which caused the separation of a considerable amount of solid material, which, by its melting point, &c., was shown to consist of dinitromesitylene. After this treatment, the oil gave on analysis correct numbers for $C_{10}H_{22}$, had sp. gr. 0·7479 at 20°, and vapour density = 4·91 (calc. 4·91). That this substance is a decane is further shown by a determination of its molecular weight by the Beckmann method, which gave 142 (calc. 142).

On subjecting the purified hydrocarbon to the action of chlorine in sunlight, a *monochlorodecane* boiling at 125—130° at 80 mm., and also a *dichlorodecane* boiling at 160—170°, were obtained.

Decane, $C_{10}H_{22}$, 173—174°.—On treating the crude distillate 169—170° with nitric and sulphuric acids, a nitro-derivative of cymene was separated. The purified hydrocarbon boils at 173—174°, has a sp. gr. 0·7467 and molecular weight, as determined by Beckmann's method, of 144; and, on chlorination, two products were obtained, a monochlorodecane boiling at 130—140° in a vacuum, and a dichlorodecane boiling at 170—171° at 80 mm.

Hendecane, $C_{11}H_{24}$, 196°, was isolated from the fraction 189—192°, which on nitration deposits a heavy nitro-compound, sparingly soluble in hot alcohol, from which solvent it crystallises in needles melting at 169—170°; the amount of the product was unfortunately insufficient for complete identification. The purified hydrocarbon boils at 196—197° at 760 mm., has sp. gr. 0·7581 and molecular weight 157 (calc. 156). By chlorination, *monochlorohendecane* boiling at 145—150° at 80 mm., and 225—230° at 747 mm., and a *dichlorohendecane* boiling at 190—200° in a vacuum, were obtained. A molecular weight determination of the monochloro-derivative gave 191, which agrees with the calculated 190.

Dodecane, $C_{12}H_{26}$, 214—216°, was obtained from the fraction of crude oil boiling between 208—210° at 730 mm. The pure substance has sp. gr. = 0·7729 and molecular weight 173 (calc. 170). It yielded a monochloro-derivative boiling at 142—153° at 20 mm., and at 230—235° under ordinary atmospheric pressure.

Ohio Petroleum.—By similar experimental data, the author shows that the composition of Ohio Trenton limestone petroleum, as regards the

members of the series C_nH_{2n+2}, is identical with that of Pennsylvanian petroleum within the same limits of temperature, but a larger proportion of aromatic hydrocarbons is present.

Canadian Petroleum.—The constituents of Canadian corniferous limestone petroleum are also the same at 163° and 173°, but the hydrocarbons collecting at 196° and 214° have a composition represented by the general formula C_nH_{2n}. The proportion of aromatic hydrocarbons is greater than in either Ohio or Pennsylvanian petroleum. There are also indications that the heavier constituents contain other substances than the aromatic hydrocarbons, but for their complete identification very large amounts of liquid would have to be dealt with.

With Canadian petroleum, it is necessary that even the earlier distillations should be done in a vacuum, not only on account of the greater quantity of sulphur compounds, but also on account of the greater proportion of unsaturated hydrocarbons and the smaller proportion of the members in question that distil between 160° and 216°. When first distilled, the fractions are colourless, but on standing they become coloured, due to the polymerisation of the unsaturated hydrocarbons, for after the removal of these bodies the oils remain colourless. The greater specific gravity of these fractions is due to aromatic constituents, and it appears probable that naphthenes are present in small amount.

Hydrocarbon, $C_{11}H_{22}$.—The portions of crude oil boiling between 188—200° were repeatedly fractionated until the largest portion came together at 196—197°. On treatment with nitric and sulphuric acids, a small amount of a nitro-compound, crystallising from alcohol and melting at 150—154°, was obtained; this melting point is near to that of dinitroisodurene (156°). After thrice repeating the purification, the oil, on analysis, gave numbers agreeing with those required for $C_{11}H_{22}$; it had a sp. gr. = 0·7729, and a molecular weight of 154 (calc. 154). The classification of this hydrocarbon is difficult; it is not an unsaturated member of the ethylene series, because it lacks additive power for the halogens, &c., and its specific gravity is much less than that of the naphthene that Markownikoff and Ogloblin separated from Russian oil at 196—197°. The substance gives a monochloro-derivative of the formula $C_{11}H_{21}Cl$, which distils at 220—228° under atmospheric pressure.

Hydrocarbon, $C_{12}H_{24}$, was obtained after repeated treatment with fuming sulphuric acid of the crude oil boiling between 208—212°. It boils at 212—214° at 745 mm., has sp. gr. = 0·7857, and gives a monochloro-derivative boiling at 160—170° in a vacuum, as well as a small amount of what appears to be a dichloro-derivative. A. W. C.

Refractive Power of Hydrocarbons [from Petroleum] and their Chlorine Derivatives. By CHARLES F. MABERY and EDWARD J. HUDSON (*Amer. Chem. J.*, 1897, **19**, 482—485).—The authors have determined the refractive power of the hydrocarbons and their chlorine derivatives mentioned in the preceding abstract. A gradual increase in refractive power is noticed with increase in boiling point, which becomes more regular after purification of the distillates. Higher values are obtained from Ohio and Canadian distillates than from

Pennsylvanian oil, analogous to the differences in specific gravity alluded to.

The quantities of the chlorine derivatives were too small to allow of complete purification, but there is a well-marked difference between the refractive power of the hydrocarbons and their monochloro-derivatives, as also between the monochloro- and dichloro-derivatives, showing the influence of the chlorine atoms. A. W. C.

Action of Alcoholic Potash on Dihalogen Derivatives. By IDA WELT (*Ber.*, 1897, **30**, 1493—1496. Compare Krafft, Abstr., 1896, i, 665).—In continuation of Krafft's work, the author has undertaken the study of the action of alcoholic potash on hexylenic bromide and heptylenic bromide, the hexylenic bromide, boiling at 78° under a pressure of 12 mm., being obtained by the addition of bromine to hexylene from β-hexylic iodide. When this bromide is boiled for 12—15 hours with its own weight of potassium hydroxide dissolved in alcohol, or heated with it in a soda-water bottle for 5—6 hours at 70°, two products are always obtained; these are easily separated by fractional distillation in an atmosphere of carbonic anhydride, the more volatile product being butylacetylene boiling at 70·5—72°; and the less volatile a monobromhexylene boiling at 46° under 20 mm. pressure. The latter, when heated at 110° for 14 hours with its own weight of potash not completely dissolved in alcohol, yields methylpropylacetylene boiling at 83°. From these facts, the author concludes that hexylene obtained from β-hexylic iodide consists, at least to a large extent, of normal hexylene, $CH_3\cdot[CH_2]_4\cdot CH{:}CH_2$. Good yields of heptylene cannot be obtained by the action of alcoholic potash on normal heptylic bromide or iodide, the chief product in both cases being ethylic heptylic ether, $C_7H_5\cdot O\cdot C_2H_5$. The best method of obtaining normal heptylene is by Krafft's method (Abstr., 1884, 571). Pure heptylic palmitate is heated in an atmosphere of carbonic anhydride at 350°, when it is decomposed into heptylene which distils over and free palmitic acid. Heptylene boils at 95° and yields a dibromide boiling at 105—107° under a pressure of 15 mm. When the dibromide is heated at 70° for several hours with its own weight of potassium hydroxide not completely dissolved in alcohol, it yields heptinene (normal amylacetylene), $C_5H_{11}\cdot C{:}CH$, boiling at 100—101°, and also a considerable quantity of unaltered monobromheptylene which is only slowly acted on when heated to higher temperatures with alcoholic potash. The author also confirms Limpricht's experiments on œnanthylidene chloride; this compound, when heated with alcoholic potash, yields normal amylacetylene and a chloroœnanthylene, $C_7H_{13}Cl$, boiling at 148°. J. J. S.

Molecular Weight of Ethylic Ferrocyanide. By GUSTAV BUCHBÖCK (*Zeit. physikal. Chem.*, 1897, **23**, 157—158).—The author determined, by the cryoscopic method, the molecular weight of ethylic ferrocyanide, a compound which dissolves readily in water without dissociation.

The values obtained varied from 316 to 333, that corresponding with the formula $(C_2H_5)_4Fe(CN)_6$ being 328, so that the ferrocyanides are represented by the simplest formula. L. M. J.

Ethereal Salts of Secondary Allylic Alcohols. By H. FOURNIER (*Bull. Soc. Chim.*, 1897, [iii], **15**, 884—889).—The following salts were prepared from ethylallylcarbinol; the acetate has already been described (Abstr., 1895, i, 198). *Ethylallylcarbinylic propionate*, obtained by the action of propionic chloride, is a colourless liquid boiling at 168—170°, and of sp. gr. 0·884 at 18°. The *isovalerate*, obtained by heating with isovaleric anhydride at 130°, is a colourless liquid boiling at 196—198°, and of sp. gr. = 0·873 at 18°. The *benzoate* is a colourless liquid boiling at 190—192° under 110 mm. pressure, or at 259—260° under atmospheric pressure, and of sp. gr. = 0·990 at 20°. The *chloride*, obtained by the action of phosphorus pentachloride, is a colourless liquid boiling and decomposing between 120° and 123°.

The following salts were prepared from isopropylallylcarbinol. The *acetate*, already described (*loc. cit.*). The *propionate*, by the action of propionic chloride, is a colourless liquid boiling at 178—180°, and of sp. gr. = 0·882 at 18°. The *isovalerate* is a colourless liquid boiling at 205—207°, and of sp. gr. = 0·870 at 18°. The *chloride*, by the action of phosphorus pentachloride, is a colourless liquid boiling with decomposition between 125 and 130°. The *sulphate*, $CH(C_3H_7)(C_3H_5)\cdot SO_4H$, is produced by the action of the alcohol on excess of sulphuric acid at −15°. Its barium salt, which crystallises with 5 molecules of water, is a white and extremely deliquescent substance.

The following salts were prepared from isobutylallylcarbinol. The *acetate*, already described (*loc. cit.*). The *propionate*, a colourless liquid, boiling at 195—197°, and of sp. gr. 0·874 at 18°. The *isovalerate*, a colourless liquid boiling at 220—222°, and of sp. gr. 0·867 at 18°. The *benzoate*, a colourless liquid boiling at 208—211° under 110 mm. pressure and 274—277° at 760 mm., and of sp. gr. 0·966 at 20°. The *chloride*, already described (this vol., i, 233), and the *sulphate*, $CH(C_4H_9)(C_3H_5)\cdot SO_4H$; its barium salt, after standing in a desiccator for 2 months, retained 2 molecules of water. M. W. T.

Reduction of Tertiary Nitroisobutylglycerol [Nitrotrihydroxy-tert.-butane] and Dihydroxyacetoxime. By OSKAR PILOTY and OTTO RUFF (*Ber.*, 1897, **30**, 1656—1665).—When tertiary nitrotrihydroxybutane (*Compt. rend.*, **121**, 210) (10 grams) and crystallised aluminium sulphate (45 grams) are dissolved in water (300 grams), and then, while the solution is constantly stirred, gradually treated with $2\frac{1}{2}$ per cent. sodium amalgam (360 grams), the chief reduction product is tertiary *hydroxylaminotrihydroxybutane* (2-methylol-2-hydroxylaminopropandiol-1 : 3), $OH\cdot NH\cdot C(CH_2\cdot OH)_3$. After careful purification (for which see original), this compound forms colourless crystals melting at 140° (corr.). It is readily soluble in water, moderately in methylic alcohol, somewhat sparingly in warm ethylic alcohol or in acetone, and practically insoluble in ether. It turns turmeric paper brown, red litmus paper blue, and also reacts with phenolphthalein; it possesses a somewhat sweet taste, and reduces Fehling's solution in the cold. The only crystalline salt which could be obtained was the *oxalate*, $[OH\cdot NH\cdot C(CH_2\cdot OH)_3]_2,H_2C_2O_4$, which crystallises in plates, and melts and decomposes at 141°, is readily soluble in water, but only sparingly soluble in methylic or ethylic

alcohol. The *picrate* melts at 113—114° (corr.). The hydroxylamino-compound, when treated with sodium nitrite and hydrochloric acid, yields the *nitroso*-derivative, $OH\cdot N(NO)\cdot C(CH_2\cdot OH)_3$, melting and decomposing at 147°. It is readily soluble in water, also in methylic or warm ethylic alcohol, and does not reduce Fehling's solution even on warming; the nitroso-compound is relatively stable, but is completely decomposed when boiled with dilute acids. The *lead* salt decomposing at about 195°, and the *methylic* ether, $OMe\cdot N(NO)\cdot C(CH_2\cdot OH)_3$, melting at 158—160° (corr.), are both described. No crystalline products could be obtained on reducing the nitroso-compound with sodium amalgam and alcohol.

When an alcoholic solution of tertiary hydroxylaminotrihydroxybutane is continuously shaken and treated at the same time with small quantities of mercuric oxide until the latter is no longer reduced, a strong odour of formaldehyde is developed, and the clear solution, after evaporating under reduced pressure yields crystals of *dihydroxyacetoxime*, $OH\cdot N\colon C(CH_2\cdot OH)_2$. It crystallises from alcohol in pointed pyramids, melts at 84° (corr.), and is readily soluble in water or methylic alcohol, but extremely sparingly in ether. Treated with an excess of phenylhydrazine, the oxime yields the osazone previously obtained by Fischer and Tafel (Abstr., 1888, 1264) from glycerose. The authors have also been able to obtain the same oxime directly from glycerose. The oxime, when reduced according to Goldschmidt's method (Abstr., 1887, 249), yields as the chief product isopropylamine; by reducing with sodium amalgam and aluminium sulphate the corresponding *amine*, $NH_2\cdot CH(CH_2\cdot OH)_2$, was obtained in the form of its *sulphate*. This salt is extremely hygroscopic, but the *hydrochloride* is less so, and melts at 95—97°. J. J. S.

Remarkable Behaviour of Chloral Hydrate with Starch and Iodine. By EDUARD SCHÄR (*Chem. Centr.*, 1896, ii, 661; from *Pharm. Centr. H.*, **37**, 540—542).—By shaking 1 part of palm-sago starch with 1000 parts of chloral hydrate solution (10 parts of water to 7 parts of chloral hydrate) an almost clear, viscous solution is obtained which, after prolonged standing, or filtering by suction, does not give a blue coloration on addition of solid iodine or of a solution of iodine in chloral hydrate. An unfiltered solution, or one simply decanted off the sediment and containing small quantities of undissolved starch grains, gives the blue coloration on addition of iodine. On adding powdered iodine and concentrated chloral hydrate solution to pure sago-starch under similar conditions, a deep blue solution is quickly formed which rapidly becomes viscous, and contains gelatinised starch and the iodine-starch compound. If an excess of the solution of iodine in chloral hydrate is added, the iodine-starch compound separates as a deep blue, powdery sediment, and there is no perceptible swelling or solution of the starch grains. On pouring two to three times the volume of water on to the reddish-brown solution, prepared by allowing a solution of starch in chloral hydrate to stand over solid iodine, the blue coloration begins to develop at the zone of contact, and gradually spreads throughout the whole liquid. The starch undergoes no change, hence excess of chloral hydrate apparently exercises a

curious retarding influence under certain conditions on the production of the blue iodine-starch compound. E. W. W.

Action of Chloroform on Starch. By Franz Musset (*Chem. Centr.*, 1896, ii, 703—704; from *Pharm. Centr. H.*, **37**, 587—588).—If a solution of starch in zinc chloride to which chloroform has been added is allowed to stand 3 months, the whole of the starch is converted into dextrin, and the solution does not give the iodine coloration, but, on adding iodine and shaking, the iodine is dissolved by the chloroform. The iodine-starch compound is not decomposed by chloroform, but all the iodine-dextrin compounds lose their iodine on shaking with chloroform, but with greater difficulty the less the content of iodine, so that a dextrin solution withdraws iodine from a strong solution of iodine in chloroform. In this slow conversion of starch into dextrin, intermediate products are formed. On evaporating the zinc chloride solution containing chloroform and adding three times its volume of alcohol, the dextrins separate. By dissolving the precipitate, after the lapse of 48 hours, in water with addition of a drop of hydrochloric acid, again precipitating with alcohol and repeating the process twice to remove the zinc chloride, a dextrin is obtained which is insoluble in cold water but dissolves in hot. The residue obtained by evaporating the solution is not more soluble in cold water, and gives a blue coloration with iodine. The filtrate from this dextrin, after evaporation on the water bath and treatment of the residue with cold water, yields a second insoluble dextrin the properties of which are similar to those of the first. The aqueous filtrate from the second dextrin contains a dextrin resulting from the action of boiling zinc chloride and chloroform, which cannot be isolated.

Chloroform converts starch-paste into a soluble modification similar to that obtained by the action of hydrochloric acid, and on heating a mixture which has stood some months, the starch dissolves and separates as a fine paste on cooling. E. W. W.

Compound of Silver Chloride and Methylamine. By R. Jarry (*Compt. rend.*, 1897, **124**, 963—965).—Silver chloride dissolves readily in liquid methylamine prepared from the carefully purified hydrochloride, and the syrupy solution, when evaporated, yields birefractive crystals of a compound $AgCl,NH_2Me$. The same compound is formed by the action of gaseous methylamine on silver chloride at the ordinary temperature. Its dissociation pressures are as follows:

T.	0°	16·8°	20·5°	32°	41°	51°	61°	65°
Pressure	9	32	43	92	168	312	584	755 mm.

The solubility of silver chloride in an aqueous solution of methylamine varies with the temperature, and a solution saturated at 20° deposits birefractive crystals which are not silver chloride. The author is investigating the conditions under which the methylamine and silver chloride combine and dissociate. C. H. B.

Correction [Ethanolamines]. By Ludwig Knorr (*Ber.*, 1897, **30**, 1492. Compare this vol., i, 313, 314).—The author corrects the

numbers previously given for the molecular dispersions of the three ethanolamines. The correct figures are ethanolamine (amidoethylic alcohol), 0·41; diethanolamine, 0·67; triethanolamine, 1·07.

J. J. S.

Methylguanidine. By N. A. Orloff (*Chem. Centr.*, 1896, ii, 662; from *Pharm. Zeit. Russ.*, 35, 513—514).—This compound, which Brieger has obtained as a ptomaine from putrefying meat, is prepared from the creatinine of urine, as follows. The urine, to which sodium acetate has been added, is precipitated by mercuric chloride solution and the washed precipitate boiled with water, calcium hydroxide, and freshly precipitated mercuric oxide in order to oxidise the creatinine to methylguanidine and oxalic acid. By saturating the solution with picric acid, concentrating and leaving it for some time, long, silky, yellow crystals of methylguanidine picrate are obtained, and may be split into their components by recrystallisation from hot water and treatment with lead hydroxide or quinine.

This method serves also as a good test for the presence of creatinine in urine.

E. W. W.

Action of Hydrogen Sulphide on Trimethyltrimethylenetriamine. By Marcel Delépine (*Bull Soc. Chim.*, 1897, [iii], 15, 889—891).—When hydrogen sulphide is passed into trimethyltrimethylenetriamine, the liquid separates into two layers. The upper layer, which remains liquid and is soluble in water, consists of methylamine hydrosulphide; the lower layer, which solidifies, is thialdine, a white, crystalline substance which has been described by Wohl. The reaction may be represented by the equation:

$$\begin{array}{l} CH_2{\cdot}NMe{\cdot}CH_2 \\ NMe{\cdot}CH_2{\cdot}NMe \end{array} + 2H_2S = \begin{array}{l} CH_2{\cdot}NMe{\cdot}CH_2 \\ S{-}CH_2{-}S \end{array} + 2NH_2Me.$$

This confirms the formula given by Wohl, on one hand, and by Brochet and Cambier (Abstr., 1895, i, 641), on the other, to thialdine and trimethyltrimethylenetriamine.

M. W. T.

Action of Carbon Bisulphide on Trimethyltrimethylenetriamine. By Marcel Delépine (*Bull. Soc. Chim.*, 1897, [iii], 15, 891—899).—*Dimethylformocarbothialdine.*—Carbon bisulphide reacts with trimethyltrimethylenetriamine with development of heat, forming a compound soluble in alcohol and melting at 96° which is isomeric with carbothialdine, produced by the action of carbon bisulphide on aldehyde-ammonia. Its constitution is represented by the formula $CS_2(CH_2NMe)_2$; in presence of hydrochloric acid, it breaks up into carbon bisulphide, formaldehyde, and methylamine. If an alcoholic solution is used, diethylic methylenic ether is formed. This substance, together with methylamine hydriodide and the hydriodide of a base, $C_4H_9NS_2$, is produced by the action of methylic iodide on a solution of dimethylformocarbothialdine in alcohol.

Dimethylic methylimidothiocarbonate, $NMe\!:\!C(SMe)_2$, is produced from the iodide mentioned above. It is a liquid heavier than water, in which it is insoluble; it is very soluble in organic solvents and boils

without decomposition at 192°. The hydriodide is very soluble in water and somewhat soluble in alcohol. It melts at 142°.

The constitution of this substance is discussed at some length.

M. W. T.

Diethylformocarbothialdine. By MARCEL DELÉPINE (*Bull. Soc. Chim.*, 1897, [iii], **15**, 899—900).—By the action of carbon bisulphide on the compound $CH_2\colon NEt$, or its polymeride, $(CH_2\colon NEt)_3$, diethylformocarbothialdine, $CS_2,2CH_2\colon NEt$, is produced. It melts at 55°, and reacts with methylic iodide to yield dimethylethylimidothiocarbonate, which boils at 200°. M. W. T.

Derivatives of Acetal. By JULIUS HESSE (*Ber.*, 1897, **30**, 1438—1442).—When α-naphthol is heated with alcoholic potash and chloracetal, it yields *α-naphthofurfuran*, $C_{10}H_6<^{CH}_{O}>CH$, which melts at 59° and boils at 288° (uncorr.). The *β-compound* melts at 65° and boils at 280° (uncorr.). When a solution of sodium in alcohol is employed instead of alcoholic potash, however, a naphthoxyacetal is produced. *β-Naphthoxyacetal*, $C_{10}H_7\cdot O\cdot CH_2\cdot CH(OEt)_2$, boils at 240° (pressure = 60 mm.) and is slightly volatile with steam. *Paratolyloxyacetal*, $C_7H_7\cdot O\cdot CH_2\cdot CH(OEt)_2$, is formed both with sodium ethoxide and alcoholic potash and boils at 262—263° (uncorr.). When boiled with water, it yields *paratolyloxyacetaldehyde hydrate*, which crystallises in slender, white needles melting at 65°. The corresponding *aldehyde* is a thick liquid, distilling at about 150°, which yields a *phenylhydrazone*, melting at 106°. *Paratolyloxyacetaldoxime* crystallises from alcohol in rhombic tablets melting at 68°. The hydrate is converted by digestion with silver oxide into paratolyloxyacetic acid.

Metatolyloxyacetal boils at 262—263° (uncorr.); the *aldehyde hydrate* melts at 56°. The *phenylhydrazone* melts at 72° and the *oxime* at 82°.

Moniodo-acetal is obtained by the action of iodine and iodic acid on acetal, and is a colourless liquid of sp. gr. 1·4944 at 15°, and boils at 100° (pressure = 70 mm.), but decomposes at higher pressures. It was not found possible to replace the halogen atom of this compound, or of chloracetal, by the cyanogen group. A. H.

Disubstituted Amidoacetal and the Preparation of Homologues of Betaine and Choline. By RICHARD STOERMER and FRIEDRICH PRALL (*Ber.*, 1897, **30**, 1504—1514).—In this research, the tertiary acetal bases were prepared partly from the secondary amines and chloracetal, and partly by the Hofmann reaction from the alkylammonium hydroxides; by converting the halogen alkyl additive products of the acetal bases into the corresponding aldehydes and oxidising with silver oxide, homologues of betaine were produced, whilst on reduction with sodium amalgam higher cholines were formed.

Diethylamidoacetal, $NEt_2\cdot CH_2\cdot CH(OEt)_2$, from monochloracetal and diethylamine, boils at 194—195°, and its *hydrochloride* is extremely deliquescent; the hydrochloride of *diethylamidoacetaldehyde*,

$$NEt_2\cdot CH_2\cdot CHO,HCl,$$

is formed from the acetal on treating it with hydrochloric acid by E. Fischer's method. It takes up water readily from moist air and melts

at 111—112°; the *aurochloride* melts at 96°, the *platinochloride* at 156°, and the *picrate* at 104°.

Methylethylamidoacetal, $NMeEt\cdot CH_2\cdot CH(OEt)_2$, prepared through the ammonium hydroxide, is a colourless, mobile liquid boiling at 179—180° and yielding a yellow *aurochloride* melting at 61°, and a fine, yellow *picrate* melting at 89°.

Triethylacetaldehydeammonium chloride, $NEt_3Cl\cdot CH_2\cdot CHO$, obtained from the ethiodide of diethylamidoacetal (m. p. 78°) by the action of freshly precipitated silver chloride, consists of reddish-yellow crystals melting at 87—88°, and giving a bright yellow, crystalline *aurochloride* melting at 140°, a *platinochloride* decomposing at 198° and crystallising with $2H_2O$, and a yellow *picrate* melting at 204°. On treating this ammonium chloride with freshly precipitated silver oxide, *ethylbetaine* or *triethylglycocine*, $CH_2{<}\genfrac{}{}{0pt}{}{-CO-}{NEt_3}{>}O$, is produced; this forms delicate, white crystals which are extremely deliquescent; the *aurochloride* crystallises in large, yellow needles melting at 211—212°, and the *platinochloride* in thick, orange-yellow needles containing $4H_2O$ and melting at 110—112°; when dehydrated it, melts and decomposes at 205—206°. *Ethylchloline hydrochloride*,

$$OH\cdot CH_2\cdot CH_2\cdot NEt_3Cl,$$

is obtained from the compound above-mentioned on reduction with sodium amalgam in acid solution; it yields a *platinochloride* melting and decomposing between 212° and 216°.

Dipropylamidoacetal, $NPr_2\cdot CH_2\cdot CH(OEt)_2$, prepared as above, is a colourless liquid boiling at 223°, the *hydrochloride* of which cannot be obtained in a crystalline condition; the *aurochloride* is an oil, the *methiodide* forms yellowish-white crystals melting at 79—80°; the *hydrochloride* of *dipropylamidoacetaldehyde*, $NPr_2\cdot CH_2\cdot CHO,HCl$, melts at 111—112°, and forms an *aurochloride* melting at 73—74°, a *platinochloride* melting at 86°, and a *semicarbazone* crystallising from ether in white crystals melting at 147°; *tripropylacetaldehydeammonium chloride*, $NClPr_3\cdot CH_2\cdot CHO$, forms feather-like crystals melting at 95—96°, and yields an *aurochloride* melting at 135°, and a *platinochloride* melting and decomposing when anhydrous at 180—183°; *propylbetaine* or *tripropylglycocine*, $CH_2{<}\genfrac{}{}{0pt}{}{-CO-}{N(Pr)_3}{>}O$, crystallises in slender, white needles melting at 184°, and yields an *aurochloride* melting at 116°, and a *platinochloride*, with $2H_2O$, melting at 90—95°.

Methylpropylamidoacetal, $NMePr\cdot CH_2\cdot CH(OEt)_2$, boils at 193—195°, its *aurochloride* melts at 38—39° and the *picrate* at 93°; the *methiodide* consists of very deliquescent, quadratic prisms.

Dimethylamidoacetal, $NMe_2\cdot CH_2\cdot CH(OEt)_2$, boils at 170—171°, and yields an *aurochloride* melting at 78—79°, a *platinochloride* melting at 92°, and a *picrate* melting at 80°; *dimethylamidoacetaldehyde*,

$$NMe_2\cdot CH_2\cdot CHO,$$

a brownish oil, forms a crystalline *platinochloride* melting at 121—122° and a *picrate* melting at 96°. J. F. T.

Some Amidoketones. By L. Behr-Bregowski (*Ber.*, 1897, 30, 1515—1525).—*Methyl amidohexyl ketone*, $C_5H_{11}\cdot CH(NH_2)\cdot CO\cdot CH_3$,

which is best prepared from methyl isonitrosohexyl ketone, yields a *hydrochloride* crystallising in fine, white needles melting at 110—112°, and a *picrate* melting at 80—85°; with potassium thiocyanate, the hydrochloride yields *αβ- or βα-methylamylimidazolyl mercaptan*, forming white, microscopic needles melting at 224°, and this, on oxidation, gives the *αβ- or βα-methylamylimidazole*, $C_3N_2HMe{\cdot}C_5H_{11}$. The latter yields a crystalline *platinochloride* melting and decomposing after recrystallisation from alcohol at 181—183°, and an *aurochloride* melting at 137—138°; the *free base* could not be obtained in the crystalline condition. Potassium cyanate reacts with methyl amidohexyl ketone hydrochloride, forming *methylamylimidazolone*, $CO{<}\begin{matrix}NH{\cdot}CMe\\ NH{\cdot}C{\cdot}C_5H_{11}\end{matrix}$, which crystallises from dilute alcohol in white, glistening scales melting and decomposing at 243°. Methyl amidohexyl ketone, on oxidation with mercuric chloride, yields *dimethyldiamylpyrazine*, $C_4N_2Me_2(C_5H_{11})_2$; this forms a *platinochloride* crystallising from alcohol in yellow, rhombohedra melting at 225—231°.

In the same way, *isoamylisonitrosoacetone*,

$$CHMe_2{\cdot}CH_2{\cdot}CH_2{\cdot}C(NOH){\cdot}CO{\cdot}CH_3,$$

a yellow solid of low melting point, yields, on reduction, *isoamylamidoacetone*, $C_5H_{11}{\cdot}CH(NH_2){\cdot}CO{\cdot}CH_3$, which separates from its alcohol solution in small, white needles melting at 123—125°; it yields a *picrate* melting at 128—129°. With potassium thiocyanate, the hydrochloride of the base yields *αβ- or βα-methylisoamylimidazolyl mercaptan*, $\begin{matrix}C_5H_{11}{\cdot}C{-}N\\ CH_3{\cdot}C{\cdot}NH\end{matrix}{>}C{\cdot}SH$, or $\begin{matrix}C_5H_{11}{\cdot}C{\cdot}NH\\ CH_3{\cdot}C{-}N\end{matrix}{>}C{\cdot}SH$, forming red crystals melting and decomposing at 255°; whilst, on oxidation, it is converted into *αβ- or βα-methylisoamylimidazole.* This crystallises in small, white quadratic prisms melting at 131—132°; the *aurochloride* melts at 156°, and the *platinochloride* at 191—192°. *Methylisoamylimidazolone*, $\begin{matrix}C_5H_{11}{\cdot}C{\cdot}NH\\ CH_3{\cdot}C{\cdot}NH\end{matrix}{>}CO$, crystallises from alcohol in long, glistening needles melting and decomposing at 271°.

Phenyl amidoethyl ketone, $NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}C_6H_5$, obtained from phenyl isonitrosoethyl ketone by reduction, separates from concentrated hydrochloric acid in large, white crystals melting at 223—225°, the *hydrochloride* forms microscopic needles which melt at 183—184°, the *platinochloride*, red prisms melting at 195—200°, and the *picrate* yellow needles melting at 160; with potassium thiocyanate, it yields *αβ- or βα-phenylmethylimidazolyl mercaptan*, $\begin{matrix}CPh{\cdot}NH\\ CMe{-}N\end{matrix}{>}C{\cdot}SH$, a substance crystallising from dilute alcohol in white, microscopic prisms, melting at about 300°. *Phenylmethylimidazole*, $\begin{matrix}CPh{\cdot}NH\\ CMe{-}N\end{matrix}{>}CH$, crystallises from ether in yellow, transparent plates melting at 178°, and yielding a *platinochloride* melting at 214—215°, an *aurochloride* melting at 188—190°, and a *picrate* which forms fine, yellow needles melting at 196°; *phenylmethylimidazolone*, $\begin{matrix}CPh{\cdot}NH\\ CMe{\cdot}NH\end{matrix}{>}CO$, from the ketone and

potassium cyanate, forms glistening leaflets melting at 285—286°; *phenyl benzamidoethyl ketone*, $C_6H_5 \cdot CO \cdot CHMe \cdot NHBz$, is obtained from the amidoketone and benzoic chloride; it crystallises from dilute alcohol in well-formed rhombohedra melting at 103°. On reduction, it gives *phenylbenzamidoethylcarbinol*, $OH \cdot CHPh \cdot CHMe \cdot NHBz$, a substance crystallising from 80 per cent. alcohol in small, white needles melting at 136—138°. J. F. T.

Cerotic Acids and Cerylic Alcohol. By ROBERT HENRIQUES (*Ber.*, 1897, **30**, 1415—1418).—Chinese wax is produced on the Chinese ash (*Fraxinus Chinensis*) by *Coccus ceriferus* (Fabr.), and consists for the most part of cerylic cerotate (Brodie, *Annalen*, 1848, **67**, 199); the author's investigation of this substance points to the formula $C_{52}H_{104}O_2$ as representing the composition, and he regards cerotic acid and cerylic alcohol as having the formulæ $C_{26}H_{52}O_2$ and $C_{26}H_{54}O$ respectively. Brodie's formulæ are $C_{27}H_{54}O_2$ and $C_{27}H_{56}O$, whilst T. Marie, who has prepared numerous compounds of this series (compare Abstr., 1896, i, 346, and this vol., i, 266), represents them by the expressions $C_{25}H_{50}O_2$, and $C_{25}H_{52}O$ respectively; the identity of the acids obtained from Chinese wax and from beeswax has not, however, been established absolutely. M. O. F.

The Benzylimides of Malic Acid. By ALBERT LADENBURG and W. HERZ (*Ber.*, 1897, **30**, 1582—1584. Compare this vol., i, 138.)—Two isomeric benzylmalimides have been described by Giustiniani (Abstr., 1892, 820), the α-modification being less soluble in water than the β-compound. Investigation of these substances from the point of view of optical rotation has led the authors to the conclusion that only one benzylimide of active malic acid exists, the so-called α-benzylmalimide being a mixture of the imide of the active acid, which is readily soluble in water, with the sparingly soluble imide of the inactive acid. M. O. F.

New Method of preparing Mesotartaric Acid and the Imides. By G. MEISSNER (*Ber.*, 1897, **30**, 1574—1578).—Treatment with boiling alkali reduces the activity of tartaric acid, and the author has therefore studied the conditions under which this change reaches a maximum, and finds that when 100 grams of tartaric acid is heated with 350 grams of caustic soda (13 mols.) and 700 grams of water in a copper flask during 8 hours, the angle of rotation in a 10 per cent. solution drops to 0·05°; the product, however, is mainly racemic acid, the yield of mesotartaric acid amounting to only 1·3 per cent. Better results are obtained by Jungfleisch's method, which consists in heating tartaric acid (30 grams) with water (4 grams) in sealed tubes at 165—170°; controlling the temperature at 160—165°, the author has obtained 5·5 per cent. by this method.

The methylimide and ethylimide of mesotartaric acid have not been obtained; the hydrogen ethylamine salt loses water at 150—155°, and yields the ethylimide of racemic acid, which melts at 173° (compare this vol., i, 140). The hydrogen propylamine salt undergoes no change at 160°, but when heated with zinc chloride during 4 hours at 125° yields a pro-

duct which may be the amido-acid $COOH\cdot CH(OH)\cdot CH(OH)\cdot CO\cdot NHPr$. The hydrogen benzylamine salt undergoes condensation when heated at 150—165°, yielding racemimide (m. p. 167°) and the *benzylimide* of mesotartaric acid, which crystallises from water in lustrous leaflets and melts at 123—126°. M. O. F.

α-Sulphocaproic Acid and its Salts. By BÉLA VON BITTÓ (*Ber.*, 1897, **30**, 1642—1648).—The author has obtained α-sulphocaproic acid by the action of ammonium sulphate on ethylic α-bromocaproate. The ethylic salt is heated with $2\frac{1}{2}$ times its weight of ammonium sulphate for 20 to 24 hours, and the small quantity of the ethylic bromocaproate which remains unacted on can be removed by extracting with ether; the aqueous solution, which contains the sulphonic acid in the form of its ammonium salt, is then boiled with lead oxide and the solution of the pure lead salt decomposed with sulphuric acid. In later experiments, it has been found more advantageous to isolate the acid by means of its barium and not of its lead salt. *α-Sulphocaproic acid*, $C_6H_{12}SO_5 + H_2O$, is a yellow syrup which, when kept over by sulphuric acid, solidifies to an indefinite crystalline mass. It gradually turns brown when kept, owing to the liberation of sulphuric acid. It is also readily decomposed when heated to 100°. The *ammonium hydrogen* salt, $C_6H_{11}SO_5NH_4 + H_2O$; *calcium* salt $(+1\frac{1}{2}H_2O)$, and *strontium* salt $(+\frac{1}{2}H_2O)$ are very fully described. The *zinc* salt $(+H_2O)$; *cadmium* salt $(+H_2O)$; and *silver* salt are also described.

J. J. S.

Action of Carbamide and Primary Amines on Maleic Anhydride. By FREDERICK L. DUNLAP and ISAAC K. PHELPS (*Amer. Chem. J.*, 1897, **19**, 492—496. Compare Abstr., 1896, i, 471).—*Maleinuric acid*, $NH_2\cdot CO\cdot NH\cdot CO\cdot CH\colon CH\cdot COOH$, is produced when maleic anhydride and carbamide in molecular proportion are heated at 100—105° in an oil bath. The crystals are perfectly white, and melt without decomposition at 167·5—168°. Although many attempts were made, the imide of maleic acid could not be obtained in quantities sufficient for complete identification by heating either maleinuric acid alone or a mixture of maleic anhydride and urea.

Paratolylmaleamic acid, $C_6H_4Me\cdot NH\cdot CO\cdot CH\colon CH\cdot COOH$, is formed when molecular proportions of maleic anhydride and paratoluidine are dissolved in chloroform and mixed; it crystallises from alcohol in lemon-yellow needles melting at 201°.

Orthotolylmaleamic acid, prepared in a similar manner, crystallises from alcohol in bunches of thick, light yellow prisms, melting at 117·5—118°.

β-Naphthylmaleamic acid crystallises from alcohol in bright yellow needles, which, when pure, melt and evolve gas at 200°. α-Naphthylamine appears to unite readily with maleic anhydride, but the product was not analysed. A. W. C.

Preparation of Zinc Ethyl. By ARTHUR LACHMANN (*Amer. Chem. J.*, 1897, **19**, 410—411).—A modification of the Gladstone and Tribe method (Trans., 1879, 750) was employed, the zinc-copper couple being used in the form of dust; the yield varied from 70 to 90 per

cent. of the theoretical, with the sample of zinc dust used. To prepare the couple in this form, zinc dust is mixed with 12 per cent. of its weight of copper oxide, and the mixture heated in a combustion tube for 20 minutes to a dull red heat in a current of hydrogen. To prevent condensation of moisture and caking, the burners should be lighted under the whole length of the tube at once, and the nearer the temperature employed approaches the melting point of zinc the better; but, of course, the zinc must not be allowed to fuse. C. F. B.

The Hexamethylene Series. By NICOLAI D. ZELINSKY (*Ber.*, 1897, 1532—1540).—As the result of many experiments, the author concludes that it is possible to convert methylhexamethylene [methylcyclohexane] into dimethylpentamethylene by reducing the corresponding alcohol with hydriodic acid; if, however, the reduction be brought about by heating the bromide of β-methylhexamethylenic alcohol with zinc and hydrochloric acid, methylhexamethylene alone is formed.

J. F. T.

1:2-Diketopentamethylene (Cyclopentadione-1:2). By W. DIECKMANN (*Ber.*, 1897, **30**, 1470—1473).—When finely divided ethylic 1:2-diketopentamethylene-3:5-dicarboxylate (Abstr., 1894, i, 324) is boiled with dilute sulphuric acid, it is slowly converted by loss of carbonic anhydride into diketopentamethylene, $CH_2<\begin{matrix}CH_2\cdot CO\\ CH_2\cdot CO\end{matrix}$. This, when distilled under a pressure of 20 mm. in an atmosphere of carbonic anhydride, passes over at 105°. It forms colourless crystals melting at 55°, and is extremely easily soluble in water, alcohol, ether, acetone, or chloroform, but only sparingly in carbon bisulphide or light petroleum. It resembles the 1:2-diketones of the fatty series in most of its chemical properties. It is remarkably stable towards acids, but alkalis readily convert it into a quinonic substance.

The *dioxime*, which melts and decomposes at about 210°, is but sparingly soluble in the usual organic solvents. The *osazone* crystallises in dark, purple crystals, and melts at 146°. The *monanil*, obtained by the action of aniline on a solution of the diketone in aqueous alcohol, melts at 111°. *Tribromodiketopentamethylene*, obtained by the action of bromine on a boiling solution of the diketone in carbon bisulphide, crystallises from light petroleum in colourless needles, and melts at 155°. J. J. S.

Semicarbazones of Cyclic Ketones. By NICOLAI D. ZELINSKY (*Ber.*, 1897, **30**, 1541—1544).—The semicarbazones of cyclic ketones, prepared in the usual way, are well-defined, crystalline substances. The semicarbazone of *ketohexamethylene* melts at 166—167°, of *β-methylketopentamethylene* at 184—185°, of *α-methylketohexamethylene* at 193—194° (with decomposition), of *β-methylketohexamethylene* Wallach) at 180—181°, of *β-methylketohexamethylene* (Einhorn) at 191—192°, of *γ-methylketohexamethylene* at 199°, of *ketoheptamethylene* (*suberone*) at 163—164°, of *αα-dimethylketopentamethylene* (I) at 190—191°, of *αα-dimethylketopentamethylene* (II) at 184—185° (with decomposition), of *γ-ethylketohexamethylene* at 175—176°, of *αα-dimethylketohexamethylene* (I) at 197—198° (with decomposition), of *αα-dimethylketohexamethylene*

(II) at 183—184° (with decomposition), of *aa-diethylketopentamethylene* at 196—197°, and of *aa-diethylketohexamethylene* at 168—169°.

J. F. T.

Action of Sodium on Nitrobenzene. By WALTHER LÖB (*Ber.*, 1897, **30**, 1572—1574).—The action of metallic sodium on chloronitrobenzene, bromonitrobenzene, and chloronitrotoluene in ethereal solution gives rise to compounds in which sodium has probably entered the nitro-group (von Hofmann and Geyger, *Ber.*, 1872, **5**, 915); the compound from parachloronitrobenzene, a black, unstable substance, has the constitution $(C_6H_4Cl\cdot NNa)_2O$. It is now found that nitrobenzene gives rise to a similar compound, which probably has the formula $(NPhNa)_2O$, being the sodium derivative of phenylhydroxylamine anhydride.

Toluene (50 parts) is boiled with sodium (2—3 parts) in a reflux apparatus, and treated with small quantities of a solution of nitrobenzene (10 parts) in toluene (20 parts), the liquid being frequently agitated; a brownish-black substance separates, and, when perfectly dry, may be preserved without undergoing change. Water eliminates the metal from the compound, giving rise to caustic soda and an oil which has reducing properties, and quickly resinifies; benzoic chloride in ethereal solution acts on the substance in the cold, and methylic and ethylic iodides at higher temperatures.

M. O. F.

Combination of Metallic Salts with Organic Bases. By D. TOMBECK (*Compt. rend.*, 1897, **124**, 961—963).—Aniline, like ammonia, precipitates solutions of the salts of several metals. With zinc chloride, it yields very small prismatic needles of the composition

$$ZnCl_2,2NH_2Ph,$$

corresponding with the compound formed by ammonia; with cadmium chloride, it forms an analogous compound, which separates in silky needles. Both compounds are only slightly soluble in water, are non-deliquescent, but turn brown when exposed to air, and begin to decompose when heated at 100°, with liberation of aniline.

Zinc and cadmium bromides form analogous compounds with very similar properties.

Zinc and cadmium iodides yield respectively the compounds

$$ZnI_2,NH_2Ph \text{ and } CdI_2,NH_2Ph.$$

The former crystallises in very long, slender needles, and the latter in bulky prisms. They are readily affected by oxygen, and are much more soluble in hot water than in cold.

Halogen salts of other metals, and the higher homologues of aniline, as well as pyridines and amines of the paraffin series, form similar compounds.

C. H. B.

Action of Phosphorus Pentachloride on Aniline and its Salts. By J. ELLIOTT GILPIN (*Amer. Chem. J.*, 1897, **19**, 352—363). —When phosphorus pentachloride (1 mol.) is heated with aniline hydrochloride (1 mol.) for 6—8 hours at 170° in a distilling flask, hydrogen chloride is evolved, and *trichlorophosphanil*, $PCl_3{:}NPh$, sublimes on to the cool part of the bulb. This substance decomposes into phosphoric and hydrochloric acids and aniline when it is boiled with water; with

strong sulphuric acid, it yields sulphanilic acid. When aniline itself is treated with phosphorus pentachloride until no more action takes place, *chlorophosphotetranilide*, $PCl(NHPh)_4$, is formed; this substance is crystalline, and is very stable; it is unaffected by boiling with water, hydrochloric acid, or concentrated alkali, but heating with water at 180° hydrolyses it into phosphoric and hydrochloric acids and aniline. When it is heated, aniline, aniline hydrochloride, and some diphenylamine hydrochloride are given off; the black, amorphous residue contains carbon, nitrogen, and phosphorus, and is so stable that "only a small amount was decomposed when it was heated in a porcelain tube, in a current of oxygen, over the blast lamp for several hours." In consequence of the formation of this substance, the carbon in most of the compounds analysed could not be determined by combustion in the usual way; oxidation with dichromate and sulphuric acid had to be employed. When the tetranilide is treated with strong sulphuric acid, a compound, $OH\cdot P(NH\cdot C_6H_4\cdot SO_3H)_4$ is formed; this is very soluble in water, and so are its *barium* and *lead* salts, in both of which the metal appears to have replaced three-fourths of the hydrogen of the SO_3H groups.

Two additional compounds are formed when phosphorus pentachloride acts on aniline. The three toluidines also yield compounds analogous to chlorophosphotetranilide. C. F. B.

Some Reactions of Metadimethylamidophenol. By LÉON LEFÈVRE (*Bull. Soc. Chim.*, 1897, [iii], 15, 900—904).—A criticism of Rothenburg's description of the reaction of this substance (Abstr., 1895, i, 538). M. W. T.

Ethylidenediphenamine [Ethylidenedianiline]. By ALEXANDER EIBNER (*Ber.*, 1897, 30, 1444—1450).—Aniline readily reacts with acetaldehyde, either in aqueous solution or in the presence of alkali, to form *ethylidenedianiline*, $CHMe(NHPh)_2$, which is extremely unstable in the moist or impure state, but when pure crystallises in colourless, lozenge-shaped tablets which melt at 51°. It is completely decomposed by acetic anhydride, but reacts with a second molecule of acetaldehyde to form an amorphous, sparingly soluble substance which probably has the formula $CHMe<{NPh \atop NPh}>CHMe$. Ethylidenedianiline is quantitatively converted by hydrocyanic acid into aniline, and the nitrile of ethylideneaniline (m. p. 92°). When it is allowed to remain in contact with water, or boiled with water or alcohol, it is converted into a mixture of the two stereoisomeric diethylidenedianilines.

It seems probable that the crystalline product described by Schiff (*Annalen*, Suppl., 3, 343) as ethylidenedianiline must have been one of its decomposition products, probably in an impure state. A. H.

Synthesis of Symmetrical Tetramidobenzene from Dinitrodichlorobenzene. By RUDOLF NIETZKI and A. SCHEDLER (*Ber.*, 1897, 30, 1666—1669).—The authors have prepared large quantities of Körner's 1 : 3-dichloro-4 : 6-dinitrobenzene (*Jahresber.*, 1875, 323) by the following method. One part of metadichlorobenzene is added to

12 parts of a mixture of fuming nitric acid (1 part) and concentrated sulphuric acid (2 parts), the mixture is kept well cooled and finally warmed for a short time on the water bath.

3 : 4 : 6-*Chlorodinitraniline*, which may be obtained by gently warming an alcoholic solution of this compound with alcoholic ammonia, crystallises in orange-yellow needles, melts at 174°, and when reduced with stannous chloride yields chlorotriamidobenzene. If, however, the dichlorodinitrobenzene is heated for 3 hours with alcoholic ammonia at 150°, both chlorine atoms become replaced by amido-groups, and Nietzki and Hagenbach's 4 : 6-dinitrometaphenylenediamine is formed (Abstr., 1887, 476). This compound, when reduced with stannous chloride, yields symmetrical tetramidobenzene. Chlorodinitrodiphenylamine $[(NO_2)_2:Cl:NHPh = 4:6:3:1]$, obtained by warming dichlorodinitrobenzene with an alcoholic solution of aniline, crystallises in orange-yellow needles and melts at 120°. *Dianilidodinitrobenzene* $[(NHPh)_2:(NO_2)_2 = 1:3:4:6]$ is obtained when dichlorodinitrobenzene is boiled with aniline; it crystallises in red prisms, melts at 186°, and when reduced yields *diphenyltetramidobenzene*,

$$C_6H_2(NH_2)_2(NHPh)_2\ [= 1:3:4:6],$$

melting at 207°. The authors have so far not been able to obtain fluorindine from this compound by the aid of oxidising agents.

J. J. S.

Non-existence of Four Phenylparatolylmethenylamidines. By HENRY L. WHEELER (*Amer. Chem. J.*, 1897, **19**, 367—374).—Contrary to Walther's statement (this vol., i, 242), only one phenylparatolylmethenylamidine exists. This melts at 103·5—104·5°, and is best made by the fourth method given by Walther, less well by the third. When the first method is employed, the product consists largely of diphenylmethenylamidine, which melts between 135° and 140°, whilst the product of the third method is largely diparatolylmethenylamidine, which melts at 140°.

C. F. B.

Hantzsch's Recent Work [Diazo-question]. By CHRISTIAN W. BLOMSTRAND (*Ber.*, 1897, **30**, 1265).—A short polemical notice on Hantzsch's communications (this vol., i, 240, 278).

J. J. S.

Migration of the Diazo-group. By ARTHUR R. HANTZSCH and FREDERICK MOLLWO PERKIN (*Ber.*, 1897, **30**, 1412—1415).—The authors have observed that when parabromodiazoamidobenzene is prepared from diazonium chloride and parabromaniline, symmetrical dibromodiazoamidobenzene is one of the products; the action of diazo nium chloride on parachlor- and paraiod-aniline proceeds in the same way, but the dihalogen compound does not arise from aniline and the substituted diazonium salt. These changes involve a partial exchange of the diazonium residue for the amido-group, a phenomenon observed for the first time by Griess (*Ber.*, 1882, **15**, 2190), and more recently by Schraube and Fritsch (Abstr., 1896, i, 221).

When an alcoholic solution of mercuric chloride is added to diazoamidobenzene dissolved in benzene, the *mercurochloride* of amidoazobenzene is produced; it separates from the mother liquor after filtration of the crystalline precipitate which is first formed, and

crystallises in reddish-yellow, lustrous plates melting at 170°. The precipitate obtained in the first instance is separable by acetone into two constituents, the soluble substance consisting of diazonium mercurochloride, whilst the insoluble portion, which is free from chloride and yields phenol under the influence of hot dilute acids, is probably a mercury derivative. M. O. F.

Diazoic Acids [Alphylnitramines]. By EUGEN BAMBERGER (*Ber.*, 1897, 30, 1248—1263. Compare Abstr., 1893, i, 327, and 1894, i, 238).—In consequence of Pinnow's recent communication on nitramines (this vol., i, 338), the author is forced to publish the work which has already been accomplished by him and his pupils.

Benzenediazoic acid, $NHPh\cdot NO_2$, is readily diazotised, nitrous acid converts it almost quantitatively into diazobenzene nitrate; this property is also characteristic of alphylnitrosohydroxylamines (Abstr., 1895, i, 217) and is shared by nitramines generally.

Benzenediazoic acid O-methylic ether, and its paranitro-derivative are acted on by nitrous acid in a similar manner. The formation of phenylazonaphthol on the prolonged boiling of a benzene solution of benzenediazoic acid and β-naphthol is attributed by the author to the previous formation of nitrous acid.

Benzenediazoic acid is readily reduced by sodium amalgam to sodium isodiazotate, and a similar reduction may be brought about by the addition of zinc dust to a solution of potassium benzenediazoate and ammonium chloride.

Parachloro-, bromo-, and methyl-benzenediazoic acids have been reduced in a similar manner, and also nitrosoalphylhydroxylamines. O-methylic benzenediazoate (Abstr., 1894, i, 238) is hydrolysed to the acid when treated with methyl-alcoholic potash (25 per cent.) and water, potassium isodiazobenzene is also formed at the same time. The isomeric N-methylic salt, phenylmethylnitramine, under similar conditions, yields no trace of either of these products. Phenylmethylnitramine reacts with alkalis in very much the same way as secondary nitramines of the fatty series (Franchmont and Erp, Abstr., 1896, i, 298), the products being aniline, nitrous and formic acids. Paranitrophenylmethylnitramine, when treated in a similar manner, yields paranitraniline and also methylparanitraniline; the latter is probably formed by some secondary reaction.

[With ROBERT DIETRICH].—*Paranitrobenzenediazoic acid* crystallises in golden-yellow needles and melts at 110—111°; its *N-methylic ether*, $NO_2\cdot C_6H_4\cdot NMe\cdot NO_2$, melts at 140° and is volatile with steam, the *ethylic ether* melts at 90°. The *O-methylic ether*, $NO_2\cdot C_6H_4\cdot N_2O\cdot OMe$, melts at 109·5° and the *O-ethylic ether* at 83°.

[With CARL SEITZ].—*Metanitrorthotoluenediazoic acid* melts at 103°; its *sodium* salt crystallises in golden needles and its *silver* salt forms a yellow precipitate. Its *N-methylic* ether melts at 70·5° and its *O-methylic* ether at 110°.

[With ALFRED VOSS].—*Orthonitrobenzenediazoic acid* crystallises in pale yellow, glistening needles, or in brownish-yellow, strongly refractive plates; it melts at 65·5° and has an extremely sweet taste. Its *N-methylic* ether melts at 67°, and is slowly volatile with steam; acids

decompose it, yielding 2 : 4- and 2- : 6-dinitromethylaniline. Its *O-methylic ether* is a brownish-yellow oil which is volatile with steam.

Metanitroparatoluenediazoic acid melts at 79° and is tasteless; its *N-methylic ether* melts at 105—105·5°, whereas the *O-ether* is a yellow oil.

[With ERNST HOFF].—*Paratoluenediazoic acid* crystallises in silver-white, glistening plates, or in glistening needles, and melts at 52—53°.

[With FRITZ STINGELIN].—*Orthotoluenediazoic acid* is a pale yellow oil, *both ethers* are also oils.

Parachlorobenezenediazoic acid melts at 81—82°, its *N-methylic ether* at 48—49°. The *silver, lead, potassium,* and *O-methyl* (oil) derivatives are also described.

Parachlororthonitrobenzenediazoic acid melts at 107—108°.

[With ARMAND STIEGELMANN].—*Parabromobenzenediazoic acid* melts at 102°, its *N-methylic ether* at 83·5—84·5°, whereas its *O-methylic ether* is an oil.

[With OTTOKAR BOECKING].—*β-Naphthalenediazoic acid,*

$$C_{10}H_7 \cdot NH \cdot NO_2,$$

melts between 131·5° and 136°; its *N-methylic ether* melts at 109°, and its *O-methylic ether* at 40°.

All the above-mentioned diazoic acids were obtained either by the oxidation of *i*- or *n*-diazotates or by the action of acetic anhydride on alphylamine nitrates. In one case, parachloraniline nitrate, the product obtained by the aid of acetic anhydride was not parachlorobenzenediazoic acid but orthonitroparachlorobenzenediazoic acid. The N-ethers were prepared from the sodium salts and the O-ethers from the silver salts. In some cases, a mixture of the two ethers was obtained, not only from the silver salt, but also from the sodium salt.

The diazoic acids and also their N-ethers are readily transformed into nitrated amines having the nitro-group in the benzene nucleus by any of the following methods. 1. By boiling with dilute mineral acids. This is not a useful method in the case of extremely stable diazoic acids. 2. By passing hydrogen chloride into a cold ethereal solution of the acid. 3. By the action of a mixture of glacial acetic acid and concentrated sulphuric acid at 0—10°. If the last method is adopted, small quantities of diazonium salts are also formed. J. J. S.

Diazoamido-compounds. By ARTHUR R. HANTZSCH and FREDERICK MOLLWO PERKIN (*Ber.*, 1897, **30**, 1394—1412).—From the fact that certain diazoamido-compounds of asymmetric structure frequently occur in two modifications, it has been conjectured that these must be represented by the tautomeric expressions $R^{I} \cdot N{:}N \cdot NHR^{II}$, and $R^{I} \cdot NH \cdot N{:}N \cdot R^{II}$; the authors describe numerous experiments for the purpose of throwing light on the properties, and conditions of production, of these isomerides.

The normal modification of parabromodiazoamidobenzene crystallises in flat, bright yellow needles, and melts at 104—105°, whether prepared from parabromodiazonium chloride and aniline, or from diazonium chloride and parabromaniline; without any apparent change in the conditions, one experiment in about four gives rise to the abnormal modification, which is produced more frequently from the first-named

pair of substances. The abnormal modifications, for several are mentioned, sometimes form pale yellow crystals, but more usually separate in granular form, and melt variously at 65°, 79°, 85°, and 87°; the solutions in alcoholic potash are frequently deep red, the less readily fusible form yielding a yellow liquid. The authors discuss, and dismiss as improbable, explanations of these facts depending on stereoisomerism, the presence of a trace of the structurally isomeric bromamidoazobenzene, the existence of an equimolecular mixture of diazoamidobenzene and dibromodiazoamidobenzene, and the occurrence of a solid solution of this mixture in bromodiazoamidobenzene; it is also unlikely that an isomeride of the type $NH<\begin{matrix}N\cdot R\\ |\\ N\cdot R\end{matrix}$ is present. They prefer to regard the substance which melts definitely at 104—105° (the normal modification) as having the constitution $NPh\!:\!N\cdot NH\cdot C_6H_4Br$, the abnormal forms most probably consisting of the isomeride $NHPh\cdot N\!:\!N\cdot C_6H_4Br$, mixed with varying quantities of the less readily fusible compound. This view is confronted by two objections, namely, the incapacity of the less definite form to undergo transformation into the normal modification, and the identical chemical behaviour of the two forms. Boiling dilute sulphuric acid resolves both modifications into parabromaniline, aniline, phenol, and parabromophenol, whilst hydrogen chloride liberates from the solutions in petroleum a mixture of diazonium and bromodiazonium chlorides. Phenylcarbimide gives rise in both cases to the bromodiazocarbamide derivative described by Goldschmidt and Molinari (Abstr., 1888, 1283); this substance melts at 131° (compare *loc. cit.*), and yields bromodiphenylcarbamide when submitted to hydrolysis.

Normal parachlorodiazoamidobenzene, $NPh\!:\!N\cdot NH\cdot C_6H_4Cl$, crystallises in golden-yellow needles and melts at 87—88°; the abnormal modification, which occurs in the same erratic manner as the bromo-derivative, usually melts at about 65°, and one preparation as low as 56—57°. The molecular refractions, determined for red light in 14·37 per cent. alcoholic solutions of the two forms, are 134·221 and 134·877 respectively. The action of phenylcarbimide on both modifications is identical.

Normal pariododiazoamidobenzene, $NPh\!:\!N\cdot NH\cdot C_6H_4I$, crystallises from petroleum in beautiful, golden-yellow needles, becoming greenish-brown under the influence of light, and melts at 118—119°; the abnormal modification is a brownish, sandy powder, which melts at 79—85°. *Paradi-iododiazoamidobenzene* melts at 165—166°.

Parachloroparabromodiazoamidobenzene, $C_6H_4Cl\cdot N\!:\!N\cdot NH\cdot C_6H_4Br$, is produced alike from chlorodiazonium chloride and bromaniline, and from bromodiazonium chloride and chloraniline, and crystallises in yellow needles melting at 138—139°; in the case of this substance, the occurrence of different modifications was not observed.

Diazoamidobenzenetoluene melts at 90—91°, and does not appear to give rise to abnormal modifications, and the same observation applies to nitrodiazoamido-compounds. M. O. F.

Formophenylhydrazide. By EUGEN BAMBERGER (*Ber.*, 1897, **30**, 1263—1264).—Formophenylhydrazide, $NHPh\cdot NH\cdot COH$, was slowly heated until a vigorous evolution of gas occurred (about 220°); after

being kept at a temperature of 190—210° for 2 hours, the mass was subjected to distillation with steam, and the residue recrystallised from alcohol. The product proved to be diphenyltetrazoline, and was in all respects identical with the compound described by Ruhemann (Trans., 1888, **53**, 850). (Compare also Pellizari, this vol., i, 231). J. J. S.

Phenylhydrazones from Aldehydes. By EMIL FISCHER (*Ber.*, 1897, **30**, 1240—1243).—The author has repeated his work on the action of phenylhydrazine on acetaldehyde, benzaldehyde, and salicylaldehyde (Abstr., 1896, i, 361) in consequence of work recently published by Causse (Abstr., 1896, i, 611). All the results previously published are confirmed, and the author concludes that all Causse's analytical results and also the speculations based thereon are absolutely false. J. J. S.

Molecular Rearrangement of the Oximes by Means of Certain Metallic Salts. By WILLIAM J. COMSTOCK (*Amer. Chem. J.*, 1897, **19**, 485—492).—Besides the ordinary reagents, the author finds that several metallic salts, notably cuprous chloride and bromide and antimony trichloride, are capable of producing the Beckmann rearrangement of an oxime into amide or substituted amide. A molecular compound of the aldoxime or ketoxime with the cuprous salt is first formed, but the change of this cuprous-haloid-oxime into an amide is not a general reaction, as in some cases the greater part of the oxime is decomposed with regeneration of aldehyde or ketone.

The tendency of benzaldoxime and acetoxime to form molecular compounds with cuprous chloride is so great that they reduce cupric chloride to cuprous chloride. A portion of the oxime is split up into the aldehyde or ketone and hydroxylamine, which latter reduces the cupric chloride to cuprous chloride with formation of nitrous acid, whilst another portion of the oxime unites with the cuprous chloride thus formed with the production of the difficultly soluble cuprous-chloride-oxime.

Cuprous chloride benzsynaldoxime, $(CHPh\colon NOH)_2,CuCl$, is formed when a cold solution of ordinary benzaldoxime in dry toluene is treated with a slight excess of cuprous chloride, and the filtered solution precipitated with light petroleum, or by mixing benzaldoxime dissolved in alcohol with an alcoholic solution of cupric chloride. It forms colourless needles, which become dark green very quickly on exposure to air, and show no sharp melting point. The copper can be removed by dilute sodium hydroxide solution, and on passing carbonic acid gas through the filtered solution benzsynaldoxime separates out.

The rearrangement of benzaldoxime into benzamide was carried out in benzene or toluene solution, the amide being obtained with sharp melting point after one crystallisation.

Cuprous bromide acts in a similar way to the chloride, but the intermediate product appears to be more stable.

Cinnamaldoxime, gives with cuprous bromide an additive product, crystallising from toluene in small, yellow needles. On boiling the toluene solution, rearrangement takes place, with production of the amide of cinnamic acid.

Œnanthaldoxime forms, with cuprous bromide in light petroleum

solution, a product crystallising in beautiful, star-like clusters of long, transparent prisms.

Cuprous chloride acetoxime, $(C_3H_6\colon NOH)_2,CuCl$, crystallises from boiling light petroleum in colourless, transparent plates or inclined prisms, which become yellow on exposure to the air, and have no definite melting point. The corresponding *cuprous bromide* compound crystallises in hexagonal plates or thick, transparent, inclined prisms melting at 121—122°. Rearrangement into methylacetamide could not be effected by boiling the toluene solution of either of these acetoxime derivatives.

Acetophenoneoxime unites with cuprous chloride in toluene solution, forming a compound which crystallises from light petroleum in thin, colourless plates which rapidly darken.

Benzophenoneoxime gives, with cuprous chloride, a compound crystallising in diamond-shaped, doubly-terminated plates of yellow colour. On boiling a toluene solution of the oxime and cuprous chloride or bromide, benzophenone is produced; but if the oxime is gradually added to antimony trichloride warmed just above its melting point, benzanilide is obtained. A. W. C.

Action of Ethylic Chloroformate on Formanilide. By HENRY L. WHEELER and H. F. METCALF (*Amer. Chem. J.*, 1897, **19**, 217—227).—The oil obtained, in addition to diphenylformamidine hydrochloride, when formanilide is treated with ethylic chloroformate, is not ethylisoformanilide, as Freer and Sherman think (Abstr., 1896, i, 611). It does not contain a trace of this substance, but consists of formylphenylurethane, together with a little phenylurethane. The gas evolved in the reaction consists of carbonic anhydride, carbonic oxide, and ethylic chloride. *Formylphenylurethane*, CHO·NPh·COOEt, may be obtained pure by treating ethylisoformanilide, OEt·CH:NPh, with a slight excess of ethylic chloroformate; it boils at 149—151° under 15 mm. pressure, gives α-formophenylhydrazide when treated with phenylhydrazine, and is readily hydrolysed to phenylurethane when boiled with alkali.

Arguments are brought forward in favour of the formula

OH·CH:NPh

for formanilide, and Claisen's reasoning (Abstr., 1896, i, 91) on behalf of the formula H·CO·NHPh is shown to be open to objection.

C. F. B.

Some Anilides of Phthalic Acid. By M. ROGOFF (*Ber.*, 1897, **30**, 1442—1443).—*Phthalanilide* melts and decomposes at 231°. When boiled with acetic acid, it yields phthalanil. *Phthalo-ψ-cumidide*, $C_6H_4(CO\cdot NH\cdot C_6H_2Me_3)_2$, melts at 227°, and crystallises in needles. *Dimethylphthalanilide*, $C_6H_4(CO\cdot NPhMe)_2$, crystallises in needles and melts at 177—177·5°. A. H.

Urethanes. By OTTO FOLIN (*Amer. Chem. J.*, 1897, **19**, 323—352).—Bromamides, when boiled with sodium methoxide in methyl-alcoholic solution, react and yield urethanes (alkyl carbamates) in accordance with the equation R·CO·NHBr + NaOMe = NaBr + R·NH·COOMe, a molecular transformation taking place not unlike the Beckmann

transformation, and that involved in the Hofmann method of preparing aliphatic amines. The bromamides were prepared by adding the amides to a solution of bromine in aqueous potassium hydroxide; they all appear to react in the manner described, alike when R is a positive radicle (Ph, $C_6H_4\cdot NO_2$, C_6H_4Br), and a more negative one ($CH_2\cdot CH_2\cdot NH\cdot COOEt$); indeed, the reaction seems well adapted for the preparation of urethanes. The new compounds obtained, with their melting points, are as follows: *Methylic metanitrophenylcarbamate*, yellow, 147—149°; *methylic orthonitrophenylcarbamate*, greenish-yellow, 53° (if the reaction is carried out at 30°, orthonitrobenzoylorthonitrophenylcarbamide, $NO_2\cdot C_6H_4\cdot NH\cdot CO\cdot NH\cdot CO\cdot C_6H_4\cdot NO_2$, is also formed; compare Swartz, this vol., i, 410); *metabromobenzobromamide*, 105°, *methylic metabromophenylcarbamate*, 84·5—85·5°; *carbomethoxy-β-amidopropionobromamide*, 117—118°. Incidentally, there were prepared *paradiethylamidobenzoic chloride*, by the action of phosphorus pentachloride on the hydrochloride of the acid (not on the acid itself, which has possibly a betaine constitution), and from this the *amide* melting at 136—137°; the ethylic salt of the acid was found to melt at 43°, whereas it has been described previously as liquid at ordinary temperatures; further, paradimethylamidobenzonitrile, also described as an oil, was found to melt at 74—76°, and it was found that, by the action of cyanogen bromide on dimethylaniline, and on parabromodimethylaniline in the presence of sodium, the product obtained in both cases was the last-named substance, no cyanide being formed.

The action of phosphorus pentachloride on urethanes was studied, usually by mixing the two substances, adding chloroform, and passing a current of hydrogen chloride through the mixture until all the phosphorus oxychloride had been carried off. The normal product of the reaction is a substituted amide of chloroformic acid, $R\cdot NH\cdot COOEt + PCl_5 = POCl_3 + EtCl + R\cdot NH\cdot COCl$, and the reaction affords a convenient method for preparing both such chloroformamides and the carbimides into which they are converted when they are heated in a current of hydrogen chloride. Chloroformometanitranilide, melting at 102°, was prepared in this way; it yields metanitrophenylcarbamide when treated with ammonia, and, when heated at 110—140° in a current of hydrogen chloride yields *metanitrophenylcarbimide;* this melts at 49—50°, is devoid of odour, and yields methylic metanitrophenylcarbamate with absolute methylic acohol, and *metanitrobenzoylmetanitrophenylcarbamide*, melting at 230°, when heated at 150° with metanitrobenz amide. Chloroformometabromanilide was also prepared; with ammonia it yields *metabromophenylcarbamide*, which softens at 162°, and melts at 164—165°. On urethane itself (ethylic carbamate), the action of phosphorus pentachloride is more complicated; instead of $NH_2\cdot COCl$, such derivatives as $PCl_2\cdot NH\cdot COCl$ or $POCl_2\cdot NH\cdot COCl$ appear to be formed. Urethane was conveniently prepared by adding a saturated solution of potassium isocyanate in 50 per cent. alcohol to an excess of strong alcoholic hydrochloric acid, and allowing the mixture to remain for 24 hours at the ordinary temperature.

The action of carbonyl chloride (phosgene) on urethane itself was studied by heating the two substances together for half an hour in a sealed tube at 75°. Three products were obtained: (1) *Chloroformyl-*

urethane, COOEt·NH·COCl, as was shown by the fact that the product of the reaction, when treated with aniline, gave ethylic phenylallophanate, COOEt·NH·CO·NHPh, melting at 106°, and identical with the substance prepared from urethane and chloroformanilide (the melting point, 120°, hitherto accepted is erroneous). (2) *Carbonyldiurethane*, $CO(NH·COOEt)_2$, which melts at 107°, yields a *mono-silver* derivative, and is a very stable substance, for it can be heated in a sealed tube for half an hour at 75—80° with a benzene solution of hydrogen chloride without undergoing any change. A better yield of this substance was obtained by heating one mol. of carbonyl chloride with two mols. of urethane and some pyridine for half an hour in a sealed tube at 85°. (3). A small quantity of ethylic allophanate $COOEt·NH·CO·NH_2$. C. F. B.

Orthocyanobenzaldehyde. By THEODOR POSNER (*Ber.*, 1897, **30**, 1693—1700).—Although meta- and paracyanobenzaldehydes may be prepared by the action of copper nitrate on the corresponding cyanobenzylic chlorides, the ortho-compound cannot be obtained in this way; the oxime, however, is obtained from orthocyanobenzylic chloride under the influence of alcoholic hydroxylamine.

Orthocyanobenzaldoxime, $CN·C_6H_4·CH{:}NOH$, crystallises from ethylic acetate and melts at 173°, resolidifying at this temperature, and subsequently fusing at 203°; it is insoluble in water, and dissolves slowly in caustic potash, yielding ammonia and phthalimide. The *hydrochloride* melts at 182°. When carefully heated with acetic anhydride, the oxime may be crystallised from this agent; but if the substances are heated together in a reflux apparatus, orthophthalonitrile is produced; this substance, when purified, is odourless (compare Pinnow and Sämann, Abstr., 1896, i, 367).

Orthocyanobenzaldoxime has the *syn*-configuration, and fusion does not convert it into the isomeric form. The phenomenon observed on melting the substance is due to the production of *orthophthalonitrilamide* (*orthocyanobenzamide*), $CN·C_6H_4·CO·NH_2$, which separates from ethylic acetate in colourless crystals and melts at 203°; alkalis convert it into phthalimide. M. O. F.

Nitrophenacetols [Nitrophenoxyacetones] and a Synthesis of 2′-Methylphenomorpholine (2′-Methyldihydrophenoparoxazine). By RICHARD STOERMER and H. BROCKEROF (*Ber.*, 1897, **30**, 1631—1641. Compare Abstr., 1887, 464).—*Paranitrophenoxyacetone*, $NO_2·C_6H_4·O·CH_2·COMe$, is best prepared by heating finely-divided potassium paranitrophenoxide (1 mol.) with chloracetone (6 mols.) for about 3 hours at a temperature just below the boiling point of the latter. The excess of the chloracetone is removed by distillation with steam, and the residue is crystallised several times from water and from alcohol. It crystallises in yellowish plates, and melts at 81°; it is readily soluble in ether or chloroform, and also in boiling water, but is less soluble in cold water or alcohol. Alkalis dissolve the compound, yielding deep yellow solutions, from which it can be recovered on acidifying. The *semicarbazone*, $NO_2·C_6H_4·O·CH_2·CMe{:}N·NH·CO·NH_2$, is sparingly soluble in water, alcohol, or ether, and melts and decomposes at 216°. The *phenylhydrazone* melting at 140°, the *oxime* melting at

119°, and the *sodium hydrogen sulphite* derivative are all described. *Orthonitrophenoxyacetone* may be obtained in a somewhat similar manner by the action of chloracetone on dry powdered potassium orthonitrophenoxide made into a cream with acetone. The mixture is first heated to 90°, and when the reaction is complete, is further heated at 115—120° for $1\frac{1}{2}$ hour. After distillation with steam, the residue is recrystallised from alcohol, and then from water. The nitrophenoxyacetone crystallises in colourless, long, silky needles, melts at 69°, and is readily soluble in the usual organic solvents. The *semicarbazone*, melting at 178°, the *phenylhydrazone*, melting at 101°, the *oxime*, melting at 102°, and the sodium hydrogen sulphite compound are all described. When reduced with tin and hydrochloric acid, orthonitrophenoxyacetone yields two bases, which may be separated by steam distillation; a considerable quantity of an oily secondary base passes over first, and then a small quantity of a tertiary crystalline base. The oily base, *2′-methylphenomorpholine*, $C_6H_4<\begin{matrix}O\text{——}CH_2\\ NH\cdot CHMe\end{matrix}$, (*2′-methyldihydrophenoparoxazine*) distils at 150—152° under a pressure of 24 mm. Its sp. gr. = 1·1148 at 15°, and its refractive index $n_{(D)} = 1·577$. When freshly distilled, the oil is quite colourless, but gradually turns yellow. The *hydrochloride*, $C_9H_{11}NO,HCl$, forms rhombic crystals readily soluble in alcohol or water. The *platinochloride*, $(C_9H_{11}NO)_2,H_2PtCl_6$, forms a yellowish-brown, crystalline precipitate, melts at 197°, and cannot be recrystallised from water or alcohol. The *carbamide*, $NH_2\cdot CO\cdot C_9NH_{10}O$, melting at 119°; *thiocarbamide* melting at 93°; *phenylcarbamide*, $NHPh\cdot CO\cdot C_9NH_{10}O$, melting at 138°; *phenylthiocarbamide* melting at 125°; *acetyl* derivative, $C_9H_{10}NOAc$, melting at 87°; *benzoyl* derivative melting at 126°; the *picrate*,

$$C_9H_{11}NO,C_6H_2(NO_2)_3OH,$$

melting at 141°, and *nitrosamine*, $C_9H_{10}NO\cdot NO$, are all described. The latter is a thick, dark-yellow oil with an odour of peppermint, and decomposes on heating; it yields a *nitronitrosamine*, $C_9H_9NO\cdot(NO)(NO_2)$, crystallising in orange-yellow, glistening crystals. This nitro-compound is sparingly soluble in cold alcohol or water, melts at 159°, and on boiling with concentrated hydrochloric acid yields *nitromethylphenomorpholine*, $C_9H_{10}NO\cdot NO_2$, melting at 132°. This nitro-compound, when reduced with tin and hydrochloric acid, yields *amidomethylphenomorpholine*, which is a brownish, strongly basic oil reacting with phenyl cyanate to form a compound melting at 207°.

The crystalline tertiary base, $C_9H_{13}NO_3$ or $C_9H_{12}NO_3$, formed at the same time as the methylphenomorpholine, melts at 106°, crystallises in colourless plates, and is extremely stable.

By reducing an alcoholic solution of orthonitrophenoxyacetone with stannous chloride at the ordinary temperature, the authors have succeeded in obtaining a small quantity of an unstable base, *α-methylphenoparoxazine*, which yields a platinochloride melting above 250°.

J. J. S.

A General Reaction of Aromatic Ketones. By SIEGFRIED BLUMENFELD and PAUL FRIEDLÄNDER (*Ber.*, 1897, **30**, 1464—1465).—When a quinone is heated with a phenol and a little dilute sulphuric acid, a colourless product is formed which is isomeric with the corre-

sponding quinhydrone. The product from α-naphthaquinone and pyrogallol melts with decomposition at 240—246° (uncorr.) and is insoluble in water. A. H.

Supposed Decompositions in the Mesitylene Series. By VICTOR MEYER and WILHELM MOLZ (*Ber.*, 1897, **30**, 1270—1277. Compare Abstr., 1896, i, 418, 419, and this vol., i, 142, 181).—The authors have been able to prove that acetomesitylene obtained by the Friedel-Craft method from pure mesitylene is absolutely pure, and contains no isomeric compound as suggested by Lucas. This has been established by the fact that the ketone on further acetylation with a large excess of aluminium chloride is completely converted into the diacetyl derivative of mesitylene. It therefore follows that no intramolecular decomposition takes place during the acetylation of mesitylene. On oxidation, acetomesitylene yields varying quantities of mesitylglyoxylic acid and symmetrical trimethylmandelic acid,

$$C_6H_2Me_3\cdot CH(OH)\cdot COOH.$$

The glyoxylic acid when subjected to dry distillation, yields practically pure mesitylcarboxylic acid; the mandelic acid when subjected to the same treatment loses oxygen and yields mesitylacetic acid,

$$C_6H_2Me_3\cdot CH_2\cdot COOH.$$

Other reactions occur at the same time, and considerable quantities of carbon and water are formed. The acid which Lucas (this vol., i, 181) regarded as prehnitic acid is therefore mesitylacetic acid, the melting points of the two acids are practically identical, but analyses of the acid obtained by distilling the mandelic acid, and also analyses of the silver salt, proved the acid to be mesitylacetic acid. J. J. S.

Gallacetophenone. By R. LÖWY (*Ber.*, 1897, **30**, 1465—1466).—*Triacetylgallacetophenone* is formed when gallacetophenone is boiled for a very short time with acetic anhydride and sodium acetate. It forms colourless, thick crystals, melts at 83° and is not coloured in alcoholic solution by ferric chloride. It is converted by bromine into *triacetylgallacetophenone bromide*, which melts at 103° and yields the same condensation products with aldehyes as the chloride. A. H.

Mesitylenediketones. By HERMANN WEIL (*Ber.*, 1897, **30**, 1285—1286).—Pavia and V. Meyer have shown that in 1 : 3 : 5-substituted hydrocarbons of the benzene series, two acetyl groups can be introduced by treatment with acetic chloride in the presence of excess of aluminium chloride, and the author has now prepared other diketones of this class, using various acid chlorides for the purpose.

Dipropionylmesitylene, $C_6HMe_3(COEt)_2$, crystallises from light petroleum in colourless aggregates melting at 101—102°, and boiling without decomposition at 327° (uncorr.).

Dibutyrylmesitylene, $C_6HMe_3(COPr^{\alpha})_2$, separates from ether in colourless crystals melting at 36°, and boiling with slight decomposition at 338—339° (uncorr.).

Di-isobutyrylmesitylene, $C_6HMe_3(COPr^{\beta})_2$, boils at 331—332° (uncorr.), and was not obtained in a crystalline condition.

Divalerylmesitylene, $C_6HMe_3(CO\cdot C_4H_9)_2$, boils at 210—211°, and slowly solidifies to colourless crystals melting at 55°.

Diœnanthylmesitylene, $C_6HMe_3(CO\cdot C_6H_{13})_2$, is a yellow oil distilling at 255° (18—20 mm.).

Attempts to form mixed compounds of this class were unsuccessful. On treating monacetylmesitylene with propionic chloride, dipropionylmesitylene is alone produced, and similarly on treating monopropionylmesitylene with acetic chloride, diacetylmesitylene is the sole product.

J. F. T.

Aromatic Thioketones and Resorcinol Dimethyl Ether [1 : 3-Dimethoxybenzene]. By GEORG HOSTMANN (*Chem. Centr.*, 1896, ii, 663—664; from *Diss. Rostock*, 1895, 1—40).—By condensation with thiophosphoryl chloride in presence of aluminium chloride, orthochloranisoil, which boils at 198—199° and is obtained from the diazo-compound of orthanisidine by means of cuprous chloride, forms lustrous, green needles of the *thioketone*,

$$CS(C_6H_3Cl\cdot OMe)_2 \ [CS : Cl : OMe = 1 : 3 : 4],$$

which melts at 178—179°, and forms a blue solution in boiling alcohol. The sulphur may be removed by means of alcoholic potassium hydroxide solution and the corresponding oxygen *ketone* obtained in white needles melting at 183—184°. By heating with powdered copper obtained by reduction, the thioketone is converted into the tetraphenylethylene derivative, $C(C_6H_3Cl\cdot OMe)_2:C(C_6H_3Cl\cdot OMe)_2$, which melts at 257°.

The following compounds are prepared similarly to the above. The thioketone of orthochlorphenetoil forms dark-green needles, and melts at 141—142°; the corresponding ketone, white needles, melts at 122—123°, and the tetraphenylethylene derivative melts at 258—259°. Orthobromanisoil boils at 208—209°, the *thioketone* forms dark-green needles, melts at 189—190°, and gives a blue solution in boiling alcohol—in this preparation an excess of water should be avoided; the corresponding *ketone* melts at 180—181°. The thioketone prepared by Rosenberg from phenylic propylic ether melts at 108—109°, and, on heating with copper, is converted into the corresponding tetraphenylethylene derivative, which forms fine needles and melts at 139—140°. The corresponding *ketone* crystallises in broad leaflets. By means of the same reaction, the thio-derivative of Michler's ketone yields lustrous crystals of the ethylene derivative, which melts at 310—315°. By reduction with sodium and alcohol, the ethylene derivative of phenetoil, which melts at 121—122°, is partially converted into the corresponding ethane derivative which, on crystallisation from glacial acetic acid, forms needles; it is insoluble in boiling alcohol, and melts at 163—164°. The ethylene derivatives of this series, containing no halogen, undergo a reaction with lead dioxide with production of a fugitive blue colour, but those containing halogens do not give this reaction. This blue compound has not been prepared in a pure state, but an intermediate product obtained by the action of lead dioxide (1 mol.) on the tetraphenylethylene derivative from anisoil (2 mols.), after crystallisation from boiling glacial acetic acid, forms colourless, transparent crystals, melts at 188—189°, and corresponds in composition to tetraphenylethylene oxide, $O<\begin{matrix}C(C_6H_4\cdot OMe)_2 \\ | \\ C(C_6H_4\cdot OMe)_2\end{matrix}$.

By the action of potassium methoxide and methylic iodide on resorcinol, the dimethyl ether, which melts at 214—220°, is the main product, but by using sodium ethoxide and a large excess of methylic iodide

and heating at 170—180° for 8 hours, products of higher boiling point are obtained. By submitting the fraction boiling at 240—250° to Gattermann and Hartmann's method of hydrolysis by means of aluminium chloride at 120°, methylic chloride and trimethylresorcinol are formed, hence this fraction contains the dimethyl ether of trimethylresorcinol (mesorcinol),

$$C_6HMe_3(OMe)_2\ [Me_3:(OMe)_2 = 1:3:5:2:4].$$

By the action of bromine, resorcinol dimethyl ether yields a dibromide which melts at 141°, and by the action of succinic anhydride in presence of aluminium chloride, dimethoxybenzoylpropionic acid,

$$C_6H_3(OMe)_2\cdot CO\cdot CH_2\cdot CH_2\cdot COOH,$$

which melts at 147°, and forms an oxime which melts at 161°. Both the acid and its oxime, when heated, form blue compounds which are probably closed chain condensation products. E. W. W.

Preparation of Metabromobenzoic Acid and Metabromonitrobenzene. By HENRY L. WHEELER and B. W. MCFARLAND (*Amer. Chem. J.*, 1897, **19**, 363—367).—Sealed tubes are not necessary in the preparation of metanitrobenzoic acid; benzoic acid (20 grams) may be heated with iron wire or gauze (6 grams) to 170° in a reflux apparatus, and in the course of 1½ hour, 48 grams of bromine (that is, a few grams more than are necessary to form the monobromo-derivative together with ferrous bromide) allowed to drop in, the temperature rising meanwhile to 260°; the yield of the pure product is nearly equal to the weight of the benzoic acid taken. If a similar experiment is carried out in a sealed tube at 225°, a much larger proportion of bromine being employed, the product is perbromobenzene, C_6Br_6.

Metabromonitrobenzene can be prepared in a similar fashion; the yield varies from 65—85 per cent. of the theoretical. Paradichlorobenzene yields a dibromo-derivative melting at 148°, presumably 1 : 4-dichloro-2 : 5-dibromobenzene. C. F. B.

Preparation of 2 : 4 : 6-Tribromobenzoic Acid from 2 : 4 : 6-Tribromaniline. By RUDOLF WEGSCHEIDER (*Monatsh.*, 1897, **18**, 217—222).—In repeating Sudborough's experiments (Abstr., 1894, i, 244), it was found that the residue insoluble in alkali, obtained in the hydrolysis of the crude nitrile, is not unchanged nitrile but consists of resin 50, 1 : 2 : 4 : 6-chlorotribromobenzene 30, and 1 : 3 : 5-trichlorobenzene 20 per cent. The last substance was probably formed by exchange of bromine for chlorine during the heating with hydrochloric acid; the second presumably in the Sandmeyer reaction, hydrochloric acid being present in the diazo-solution.

The following melting points were found: 2 : 4 : 6-tribromaniline, 120—121°; 2 : 4 : 6-tribromobenzoic acid, 188—189°; 1 : 2 : 4 : 6-chlorotribromaniline, 87—88°. C. F. B.

***c*-Durenecarboxylic Acid.** By VICTOR MEYER and WILHELM MOLZ (*Ber.*, 1897, **30**, 1277—1280).—Of the three durenecarboxylic acids, two, namely, those from durene and isodurene, have already been prepared and investigated, and the present paper deals with the preparation and properties of the third, that is, consecutive durenecarboxylic acid. This acid is not so readily prepared as its isomerides, the best

method being by the carboxylation of consecutive durene (prehnitene). This hydrocarbon (which must be quite pure, when it boils at 202—204°) on treatment with urea hydrochloride and aluminium chloride is converted into the *amide*, a substance crystallising from alcohol in glistening needles melting at 222°. On hydrolysis by means of sodium nitrite, it yields consecutive *durenecarboxylic acid* (1 : 2 : 3 : 4-tetramethylbenzenecarboxylic acid), which crystallises from light petroleum in slender, white needles melting at 168—169°; when etherified by Emil Fischer's method, it yields 97 per cent. of ethylic salt, and can by this means be readily separated from its isomerides, which, under similar conditions, are not etherified. J. F. T.

Derivatives of Parahydroxybenzoic Acid and of Anisic Acid. By KARL AUWERS (*Ber.*, 1897, **30**, 1473—1478).—The earlier descriptions of 3-chloro-4-hydroxybenzoic acid (Peltzer, *Annalen*, 1868, **146**, 286; Lössner, *J. pr. Chem.*, 1876, [ii], **13**, 432; Hasse, Abstr., 1878, 416) being so contradictory, the author has prepared it from 3-amido-4-hydroxybenzoic acid (this vol., i, 341). The acid has most of the properties given by previous authors, but melts at 165—166°; its *methylic* salt crystallises in flat needles and melts at 106—107°.

3-Iodo-4-hydroxybenzoic acid, prepared in a similar manner, crystallises in flat, glistening needles and melts at 173·5—174·5°. The author has also obtained the acid by Peltzer's method (*loc. cit.*), and finds that it then also melts at 173·5—174·5° instead of 160° as previously given. Its *methylic* salt crystallises in glistening needles and melts at 155—156°.

By reducing methylic metanitroanisate (Goldschmidt and Polonowska, Abstr., 1887, 1041) with aluminium amalgam and dilute alcohol, the author has obtained methylic metamidoanisate melting at 85—86°, and, on hydrolysis, the free acid melting at 204°, this acid being identical with the one obtained by Balbiano (*Gazzetta*, **14**, 247). The same acid is also obtained by reducing the nitro-acid with alcoholic ammonium sulphide or with tin and hydrochloric acid; in the former case, the yield is extremely poor, and the acid usually has a lower melting point (198°) owing to the presence of impurities. This accounts for the low melting points previously given by Zinin (*Annalen*, **92**, 327) and by Paternò and Oliveri (*Gazzetta*, **12**, 93). *Methylic metachloranisate*, obtained from the above methylic amidoanisate by Sandmeyer's reaction, melts at 94·5—95·5, and on hydrolysis yields the free acid melting at 213°. (Compare Schall and Dralle, *Ber.*, 1884, **17**, 2529.) J. J. S.

Some Salts of the Phthalic Acids, and the Author's Crystal-water Theory. By THEODORE SALZER (*Ber.*, 1897, **30**, 1496—1498). —The author describes various salts of phthalic, isophthalic, and terephthalic acids, and remarks that in most instances the water of crystallisation contained in them is in accordance with that demanded by his crystal-water theory. J. F. T.

Isomeric Chlorides of Paranitrorthosulphobenzoic Acid. By IRA REMSEN and G. W. GRAY (*Amer. Chem. J.*, 1897, **19**, 496—511. Compare Abstr., 1895, i, 472, 473, 474; this vol., i, 243, 244).—The

authors have succeeded in preparing both the acid chlorides of nitrosulphobenzoic acid, namely, $SO_3Cl\cdot C_6H_3(NO_2)\cdot COCl$ and

$$C_6H_3(NO_2)\genfrac{<}{>}{0pt}{}{CCl_2}{SO_2}O.$$

Paranitrorthosulphobenzoic acid is obtained by treating paranitrotoluene with fuming sulphuric acid, and oxidising the paranitrorthotoluenesulphonic acid so produced with potassium permanganate. When the potassium salt of the acid is heated at 150° with phosphorus pentachloride, both the above mentioned chlorides are produced, and are separated by their different solubilities in chloroform, or by treating the chloroform solution of the chlorides with dilute ammonia. An 80—90 per cent. yield of the *unsymmetrical chloride* is obtained which crystallises from light petroleum in fine, white needles or long, flat plates melting at 56—57° (uncorr.), and decomposing when heated above 160°. The yield of *symmetrical chloride* is from 10—20 per cent., and it forms crystals showing monoclinic pinacoids and basal plane, and melts at 94—95° (uncorr.). It can be heated in sealed tubes to 150° with phosphorus oxychloride without undergoing decomposition. Cold water acts slowly on both chlorides, but, on boiling, decomposition is complete in a few minutes, being equally rapid in both cases. Dilute potash produces potassium hydrogen paranitrorthosulphobenzoate from both chlorides.

The symmetrical chloride, on treatment with dilute ammonia, gives the ammonium salt of paranitrobenzoicsulphinide, which crystallises in rectangular plates of glistening flakes, and does not melt below the boiling point of sulphuric acid.

Paranitrobenzoicsulphinide is produced as fine needles or plates, melting at 209° (uncorr.) on adding hydrochloric acid to the above-mentioned acid potassium salt. The *methylic* and *ethylic* salts are produced on heating the sulphinide in sealed tubes with the corresponding alkylic iodide; the former crystallises in leaf-like crystals melting at 179° (uncorr.), and the latter in needles melting at 172° (uncorr.).

Paranitrocyanobenzenesulphonic Acid, $NO_2\cdot C_6H_3(CN)\cdot SO_3H$.—The unsymmetrical chloride gives the ammonium salt of this acid when treated with dilute ammonia. The free acid is formed when its silver salt is treated with hydrochloric acid or its barium salt with sulphuric acid. It crystallises in long prisms, and melts between 145—150°. On heating with caustic potash, ammonia is liberated, and then, on adding hydrochloric acid, the acid potassium paranitrorthosulphobenzoate is obtained.

Paranitrocyanobenzenesulphonic chloride, $NO_2\cdot C_6H_3(CN)\cdot SO_2Cl$, is formed when the potassium salt of the acid is treated with phosphorus pentachloride; it crystallises in long, rectangular prisms, which melt at 107—108° (uncorr.).

Paranitrocyanobenzenesulphonamide, $NO_2\cdot C_6H_3(CN)\cdot SO_2\cdot NH_2$, is formed when the acid chloride is treated with ammonia. It crystallises in small, rectangular blocks resembling cane-sugar, and does not melt below 270°.

Paranitrocyanobenzenesulphonanilide, $NO_2\cdot C_6H_3(CN)SO_2\cdot NHPh$, crystallises in fine needles, and melts at 207—208° (uncorr.).

The *silver*, *potassium*, *barium*, *calcium*, *magnesium*, and *zinc* salts of

paranitrocyanobenzenesulphonic acid and paranitrobenzoicsulphinide are also described. A. W. C.

Derivatives of Orthobenzoicsulphinide ("Saccharin"). II. By HUGO ECKENROTH and GEORG KOERPPEN (*Ber.*, 1897, **30**, 1265—1269. Compare Abstr., 1896, i, 304 and 438).—A better yield of ethylenediorthobenzoicsulphinide (*loc. cit.*) is obtained when benzoicsulphinide, ethylenic bromide, and alcohol are heated for several days in a flask, using a reflux condenser. The product is washed with alcohol to remove the bromethyl compound, and is then crystallised several times from acetic acid. The ethylene compound forms thick, glistening crystals, and melts at 245—246°.

Hydroxyethylorthobenzoicsulphinide, $C_6H_4<\begin{matrix}CO\\SO_2\end{matrix}>N\cdot C_2H_4\cdot OH$, is obtained when dilute caustic soda is carefully added to a solution of bromethylorthobenzoicsulphinide in hot water, and after some hours' heating the product acidified. It crystallises in needles, melts at 183°, and is readily soluble in alcohol, benzene, and acetic acid.

A small quantity of *methylenediorthobenzoicsulphinide* may be obtained by the action of formaldehyde and sulphuric acid on benzoicsulphinide. It crystallises in six-sided plates and melts at 290°.

Ethylic orthobenzoicsulphinidecarboxylate, $C_6H_4<\begin{matrix}CO\\SO_2\end{matrix}>N\cdot COOEt$, is a crystalline powder which melts at 136° and is readily soluble in alcohol or ether. When boiled for some time with water, it is decomposed into benzoicsulphinide, alcohol, and carbonic anhydride.

Methylic orthobenzoicsulphinideacetate, $C_6H_4<\begin{matrix}CO\\SO_2\end{matrix}>N\cdot CH_2\cdot COOMe$, melts at 118° and the *ethylic* salt at 104°. Both are readily soluble in the usual organic solvents.

Benzoylorthobenzoicsulphinide, obtained by the action of benzoic chloride on benzoicsulphinide at 225° for 2 hours, crystallises in colourless needles, melts at 165°, and is readily soluble in water and the usual solvents.

Phenoxyethylorthobenzoicsulphinide,

$$C_6H_4<\begin{matrix}CO\\SO_2\end{matrix}>N\cdot CH_2\cdot CH_2\cdot OPh,$$

crystallises in glistening cubes, and melts at 81—82°. It is insoluble in water and cold alcohol, but readily soluble in benzene, acetic acid, and hot alcohol. When warmed with sodium ethoxide, it is hydrolysed to *phenoxyethylorthoamidosulvhobenzoic acid*, melting at 139°.

This acid, when heated with concentrated hydrochloric acid for several hours, is partially reconverted into phenoxyethylbenzoicsulphinide; orthosulphobenzoic acid and phenoxyethylamine hydrochloride (Schmidt, Abstr., 1890, 372) are also formed.

Picrylorthobenzoicsulphinide, $C_6H_4<\begin{matrix}CO\\SO_2\end{matrix}>N\cdot C_6H_2(NO_2)_3$, crystallises in glistening, yellow cubes, melts at 262°, and is soluble in hot acetic acid. It is decomposed by both sodium ethoxide and hydrochloric acid, yielding picric acid and orthobenzoicsulphinide.

J. J. S.

Action of Certain Alcohols on *asym*-Metadiazoxylenesulphonic Acid. By WILLIAM B. SHOBER and HERMAN E. KIEFER (*Amer. Chem. J.*, 1897, i, 381—393).—Xylidinesulphonic acid was prepared by sulphonating α-xylidine, and diazotised by mixing it into a paste with water, passing nitrous fumes in until all had dissolved, and adding alcohol; or by passing nitrous fumes into a cooled suspension of the acid in alcohol. When it is boiled with methylic, ethylic, or propylic alcohols, either under atmospheric pressure or under a pressure of 400—900 mm. of mercury, the diazosulphonic acid always yields a little xylenesulphonic acid, but the main product is an alkoxyxylenesulphonic acid, $OR\cdot C_6H_2Me_2\cdot SO_3H$ [$OR:Me_2:SO_3H = 4:1:3:6$].

Metamethoxyxylenesulphonic acid yields *potassium*, $C_9H_{11}SO_4K + \frac{1}{2}H_2O$; *barium*, $(C_9H_{11}SO_4)_2Ba + 4H_2O$, and *copper*, $(C_9H_{11}SO_4)_2Cu + 4H_2O$, salts, and an *amide* melting at 190°. Propoxyxylenesulphonic acid yields *barium*, $(C_{11}H_{15}SO_4)_2Ba + 3H_2O$; *potassium*, $C_{11}H_{15}SO_4K + H_2O$, and *zinc* $(C_{11}H_{15}SO_4)_2Zn + 5H_2O$, salts, and an *amide* melting at 146°. These salts are yellow, except that the copper salt is green when hydrated. When the methoxyxylenesulphonamide is oxidised with permanganate, it yields two products; one, formed in small amount, melts at 270—275° and contains no nitrogen, but 34·16 per cent. of carbon; the other melts at 236—238°, and is *methoxysulphaminetoluic acid*, $COOH\cdot C_6H_2Me(OMe)\cdot SO_2\cdot NH_2 + H_2O$; its *barium* $(C_9H_{10}NSO_5)_2Ba + 7H_2O$, and *calcium*, $(C_9H_{10}NSO_5)_2Ca + 5H_2O$, salts were prepared. C. F. B.

Hydrochlorides of Diphenylhydroxyethylamine Bases. By EMIL ERLENMEYER, jun. (*Ber.*, 1897, **30**, 1525—1527).—The author contends that two bases of the formula $OH\cdot CHPh\cdot CH_2\cdot NHPh$ exist, one of which melts at 129—130° and the other at 163°. The salts of the first crystallise from water in monoclinic crystals, and from methylic alcohol in very characteristic hexagonal plates containing methylic alcohol of crystallisation, and efflorescing in the air, whilst the salts of the second crystallise either in the hexagonal or monoclinic systems. J. F. T.

Formation of Diphenylhydroxyethylamine Bases from Benzaldehyde and from Glycocine. By EMIL ERLENMEYER, jun. (*Ber.*, 1897, 1527—1531).—An explanation is given of the curious formation of diphenylhydroxyethylamine bases from benzaldehyde and from glycocine, a reaction which proceeds at ordinary temperatures. J. F. T.

Resolution of Isohydrobenzoin into its Active Components. By EMIL ERLENMEYER, jun. (*Ber.*, 1897, **30**, 1531).—Isohydrobenzoin is readily resolved into its active constituents on crystallising it from ether, the enantiomorphic crystals can thus be obtained a centimetre long, and can be easily measured. For the lævo-modification the value $\alpha_D = 7° 18'$ was found. J. F. T.

An Isomeride of Triphenylacrylic Acid, and the Conversion of the One into the Other. By VICTOR MEYER and HERMANN WEIL (*Ber.*, 1897, **30**, 1281—1284).—As already stated (Abstr., 1896, i, 146), in the preparation of triphenylacrylic acid from dichlorobenzo-

phenone and methylic phenylacetate, a bye-product is formed, which is evidently a diphenylindone of the formula $C_6H_4<\substack{CPh \\ CO}>CPh$, and it was further mentioned that on fusion with potash this substance is converted into an acid. This acid, which is an isomeride of triphenylacrylic acid, separates from glacial acetic acid in colourless crystals resembling common salt, and melting at 185—186°; it probably has the constitution $CHPh:CPh\cdot C_6H_4\cdot COOH$, or a *diphenylorthovinylbenzoic acid*, and is formed by the addition of water to the diphenylindone. Both acids are reconverted into the indone by treatment with zinc chloride, although it is not possible to change the one acid directly into the other. J. F. T.

Some Sulphonic Acids of α-Naphthol. By PAUL FRIEDLÄNDER and R. TAUSSIG (*Ber.*, 1897, **30**, 1456—1463).—The authors have found that many of the sulphonic acids of α-naphthol can be purified by means of their zinc salts, since, when syrupy zinc chloride is added to their moderately concentrated aqueous solutions, the impurities are first precipitated, and then the solid zinc salt. 1-Naphthol-2-sulphonic acid seems to be the only α-naphtholsulphonic acid which is sparingly soluble in moderately concentrated mineral acids.

Zinc 1-*naphthol*-3-*sulphonate* crystallises in long, faintly pink needles. 1-Naphthol-4-sulphonic acid is best purified by means of its *zinc* salt, which crystallises in rhombic tablets containing $8\frac{1}{2}$ mols. H_2O. The *sodium* salt crystallises in prisms. The product of the action of the calculated amount of fuming sulphuric acid on naphthol seems to be 1-naphthol-2-sulphonic acid (compare Baum, Patent B 4197 of 30th June, 1883; Claus and Oehler, *Ber.*, **15**, 312; Claus and Knyrim, *Ber.*, **18**, 1824).

Zinc 1-*naphthol*-4′-*sulphonate* crystallises in long, lanceolate needles. When sodium nitrite is added to its solution in hydrochloric acid, 2-*nitroso*-1-*naphthol*-4′-*sulphonic acid* is formed, crystallising in long, yellow, fascicular needles.

When 1-hydroxy-2-naphthol-4 : 2′-disulphonic acid is heated at 140—145° with moderately concentrated sulphuric acid, it is converted into 1-*hydroxy*-2-*naphthol*-2′-*sulphonic acid*, which crystallises in sparingly soluble, slender, white needles, and separates from a hot concentrated solution in a very characteristic gelatinous mass of microscopic needles; its aqueous solution is coloured indigo-blue by ferric chloride. The *barium* salt, $[C_{10}H_5(OH)(COOH)SO_3]_2Ba$, forms very sparingly soluble white needles. When the acid is heated with water at 120°, it loses carbonic anhydride and forms 1-naphthol-2′-sulphonic acid, as a hygroscopic, crystalline mass, which gives a brownish-violet coloration with ferric chloride. The *zinc* salt forms stellate groups of large, readily soluble needles. It combines with 1 molecule of paradiazonitrobenzene in acid solution, and with 2 molecules in alkaline solution.

The acid obtained by Gürke and Rudolph (German Patent 38281) is identical with that obtained by Freund (German Patent 27346), and has the constitution of a 1-naphthol-3 : 3′-disulphonic acid, since both of

these are converted by heating with ammonia into the same 1 : 3-naphthylendiamine-3-sulphonic acid.

1-Naphthol-2 : 4 : 2′-trisulphonic acid is characterised by its *barium* salt, which separates in very slender, glistening crystals, which are very difficult to redissolve even in boiling water. The sulphonic group in the position 4 is very easily removed by the action of sodium amalgam or sodium nitrite. This acid appears to be formed by much more dilute sulphuric acid than has hitherto been supposed, acid of 66° B. converting at least a seventh of the naphthol used into this acid at 125°. A. H.

Naphthoketocoumarin and its Condensation Products. By G. Ullmann (*Ber.*, 1897, **30**, 1466—1470).—2 : 1-Acetylnaphthol (Friedländer, Abstr., 1895, i, 668) is not readily acetylated, the best yield of the *acetate*, $C_{10}H_6Ac\cdot OAc$, is obtained when the acetylnaphthol (1 part) is heated with acetic anhydride (3—3½ parts) and anhydrous sodium acetate (1 part) until its alcoholic solution no longer gives a green colour with ferric chloride. It crystallises from its alcoholic solution in long, brownish needles, melts at 103·5°, and is readily soluble in the usual solvents. It yields no coloration with ferric chloride, and is readily hydrolysed by alkalis. 2 : 1-*Acetylnaphthylic benzoate*, $C_{10}H_6Ac\cdot OBz$, also crystallises in long, brownish needles, and melts at 96·5°.

Bromine readily reacts with an acetic acid solution of acetylnaphthylic acetate, even when the two are used in molecular proportion, yielding a 2-*bromacetylbromo*-1-*naphthol*, $OH\cdot C_{10}H_5Br\cdot CO\cdot CH_2Br$, which crystallises in yellowish needles and melts at 136·5°; bromine reacts with a benzene solution of acetylnaphthylic acetate, forming *bromacetylbromonaphthylic acetate*, $OAc\cdot C_{10}H_5Br\cdot CO\cdot CH_2Br$. This crystallises in colourless needles, melts at 124°, and is fairly readily soluble in alcohol. Both compounds are decomposed by sodium hydroxide, yielding red solutions, and both form the same condensation products with aldehydes. 2 : 1-*Bromacetylnaphthol*, obtained by the action of bromine (1 mol.) on a solution of acetylnaphthol in dry carbon bisulphide, crystallises in colourless plates and melts at 77—87°, but the compound cannot be obtained in a pure form. The naphthol, when dissolved in carbon tetrachloride, reacts with bromine, yielding a monobromo-derivative, $OH\cdot C_{10}H_6\cdot CO\cdot CH_2Br$, melting at 124·5 together with other products. When the finely-divided monobromo-derivative is warmed for a short time with caustic soda (1 mol.) and hydrochloric acid is then added, a precipitate of *naphthoketocoumarin*, $C_{10}H_6<{O \atop CO}>CH_2$, is obtained. When recrystallised from water, this melts at 91—92°; it is but slowly volatile with steam, dissolves readily in ether, and only sparingly in alcohol. On warming with Fehling's solution, it yields a magenta-red solution from which a violet-red precipitate is thrown down.

Naphthoketocoumarin (2 parts) reacts with an alcoholic solution of protocatechuic aldehyde (1 part) in the presence of concentrated hydrochloric acid, yielding a yellow, crystalline *naphthoflavone* which

melts and decomposes at 240°. It is readily purified by means of its sodium salt, which is precipitated on adding strong sodium hydroxide to its aqueous solution. The *methylenic ether* of this compound is obtained by the condensation of naphthoketocoumarin with piperonal; it crystallises in yellow needles, is sparingly soluble in the usual solvents, but dissolves more readily in acetic acid or amylic alcohol. 2 : 1-Dibromacetylnaphthol also reacts with piperonal, yielding a condensation product which crystallises in yellow needles. The author has not been successful in preparing the brominated or chlorinated acetylnaphthols by the action of brom- or chlor-acetic acid on α-naphthol in the presence of zinc chloride. With phosphorus oxychloride, a *chloracetyl* compound melting at 48° was obtained.

J. J. S.

Odorous Constituents of Oil of Celery. By GIACOMO L. CIAMICIAN and PAUL G. SILBER (*Ber.*, 1897, **30**, 1419—1424. Compare this vol., i, 291).—The authors have definitely established the formula $\begin{matrix} CH_2\cdot CH_2\cdot CH\cdot CO\cdot C_4H_9 \\ CH_2\cdot CH{=}C\cdot COOH \end{matrix}$ for sedanonic acid, which is therefore orthovaleryl-Δ^1-tetrahydrobenzoic acid; sedanolic acid, on the other hand, is orthohydroxyamyl-Δ^5-tetrahydrobenzoic acid,

$$\begin{matrix} CH_2\cdot CH : C\cdot CH(OH)\cdot C_4H_9 \\ CH_2\cdot CH_2\cdot CH\cdot COOH \end{matrix},$$

the experiments on which these conclusions are based being described in the following abstracts. The odoriferous constituents are sedanolide, $C_6H_8{<}{\begin{matrix}CH(C_4H_9)\\CO\end{matrix}}{>}O$, and an anhydride of sedanonic acid,

$$C_6H_8{<}{\begin{matrix}C(:C_4H_8)\\CO\end{matrix}}{>}O;$$

the former substance is butylphthalide, and it is interesting to notice that hydrogenised phthalylisopropylidene, which probably has the constitution $C_6H_4{<}{\begin{matrix}CHPr\\CO\end{matrix}}{>}O$, has an odour which suggests celery oil.

M. O. F.

Sedanonic Acid. By GIACOMO L. CIAMICIAN and PAUL G. SILBER (*Ber.*, 1897, **30**, 1424—1427. Compare the preceding abstract).—*Orthohydroxyamylhexahydrobenzoic acid* (*2^1-pentylolcyclohexanemethylic acid*), $COOH\cdot C_6H_{10}\cdot CH(OH)\cdot C_4H_9$, is prepared by reducing sedanonic acid with sodium and alcohol, and crystallises in needles; it is identical with the product from sedanolic acid, and after repeated crystallisation from ethylic acetate melts at 131°. When the substance is treated with boiling acetic chloride, and the agent evaporated, a colourless oil is produced having the odour of oil of celery; this substance is probably hexahydrobutylphthalide, $C_6H_{10}{<}{\begin{matrix}CH(C_4H_9)\\CO\end{matrix}}{>}O$, and yields the acid when hydrolysed with caustic alkali.

Cold solutions of sedanonic acid are indifferent towards sodium amalgam; when heated with this agent, however, the *acid* $C_{12}H_{20}O_3$ is produced, yielding an amorphous *silver* salt.

When sedanonic acid is oxidised in alkaline solution with potassium permanganate, oxalic, glutaric, and normal valeric acids are produced.

M. O. F.

Sedanolic Acid and Sedanolide. By GIACOMO L. CIAMICIAN and PAUL G. SILBER (*Ber.*, 1897, **30**, 1427—1433. Compare the foregoing abstracts).—*Orthohydroxyamylbenzoic acid* (*2*[1]*-Pentylolphenmethylic acid*), $COOH\cdot C_6H_4\cdot CH(OH)\cdot C_4H_9$, is obtained by oxidising sedanolide in alkaline solution with potassium permanganate, and separates in aggregates of small needles on adding petroleum to the ethereal solution; it melts at 71—72°, and readily undergoes conversion into the anhydride, *butylphthalide*, which has the odour of celery oil, and boils at 177—178° under a pressure of 15 mm. Phenylglyoxylcarboxylic acid is another product of the oxidation of sedanolic acid; the acidic filtrate from orthohydroxyamylbenzoic acid contains the products of ring hydrolysis, oxalic, succinic, and normal valeric acids.

Hydrosedanolidecarboxylic acid, $C_{13}H_{20}O_4$, is obtained by the action of alcoholic potassium cyanide on sedanolide, and hydrolysing the nitrile produced (compare Bredt and Kallen, this vol., i, 154); the *silver* salt is amorphous.

Reduction of sedanolic acid with sodium and alcohol gives rise to orthohydroxyamylhexahydrobenzoic acid, obtained in the same way from sedanonic acid (foregoing abstract).

M. O. F.

Action of Ethylic Oxalate on Camphor. II. By J. BISHOP TINGLE (*Amer. Chem. J.*, 1897, **19**, 393—409. Compare Trans., 1890, 652).—Ethylic camphoroxalate, $C_8H_{14}<\begin{matrix}CH\cdot CO\cdot COOEt \\ | \\ CO\end{matrix}$, is best prepared by dissolving camphor ($1\frac{1}{2}$ mol.) and ethylic oxalate (1 mol.) in light petroleum, adding sodium wire (1 atom), boiling for about half an hour in a reflux apparatus, and allowing to remain for 24 hours; the yield is about 75 per cent. of the theory, and 17 per cent. of the acid itself is obtained besides. It will not yield a copper salt, and appears to have no acid properties; it is readily hydrolysed by aqueous sodium hydroxide in the cold; when heated, it decomposes for the most part into alcohol and the acid, no doubt by the agency of traces of water, and the remainder is further decomposed into camphor and ethylic hydrogen oxalate, which is yet further resolved into ethylic formate and carbonic anhydride. Its phenylhydrazone, when purified by recrystallisation, melts at 212°, and not at 187—188° as previously stated; by mixing it with half the amount of alcohol necessary for complete solution, and passing in hydrogen chloride at 0° until all has dissolved, *ethylic camphylphenylpyrazolecarboxylate*, $C_8H_{14}<\begin{matrix}C\cdot C(COOEt) \\ \| \\ C\text{——}NPh\text{——}\end{matrix}>N$, melting at 114°, is obtained (the same condensation takes place at a higher temperature under the influence of acetic anhydride); this substance is readily hydrolysed by alcoholic potash to the free *acid*, which melts at 197° when dry. Camphoroxalic acid is found to crystallise in hexagonal forms, like those of quartz; with a large excess of hydroxylamine, it yields an additive *compound*, $C_8H_{14}<\begin{matrix}CH\cdot C(OH)\cdot COOH \\ |\quad\quad | \\ CO\quad NH\cdot OH\end{matrix}$, which melts and decomposes at 146·5°,

and, when heated with acetic anhydride and acetic acid, yields *camphylisoxazole*, $C_8H_{14}<\begin{matrix}C\cdot CH \\ \| \\ C-O\end{matrix}>N$, melting at 124—125°.

C. F. B.

Pyrethrin, the Active Principle of the Root of Anacyclus Pyrethrum Dec. By AUGUST SCHNEEGANS (*Chem. Centr.*, 1896, ii, 945—946; from *Pharm. Zeit.*, 41, 668).—In order to prepare pure pyrethrin, the triturated root is boiled several times with alcohol, and the extract, after driving off the alcohol, is treated with absolute alcohol, whereby a large quantity of a grey, tasteless tar is separated. With alcoholic lead acetate solution, a yellow precipitate is formed; this is removed, the filtrate freed from lead by hydrogen sulphide, evaporated, and the reddish-yellow syrup freed from tar by dissolving in ether and evaporating to dryness with addition of milk of lime and sand. The solid powdered mass is extracted with light petroleum and the light yellow solution so obtained freed from a brown, tasteless oil by shaking with sodium hydroxide solution, evaporated and finally crystallised by drying over sulphuric acid in a vacuum. By draining and washing with a little ether, the crystals may be cleansed from the adherent dark oil. *Pyrethrin* forms white, clustered needles, melts at 45°, and has an extremely burning taste. It is very easily soluble in absolute alcohol, ether, benzene, glacial acetic acid, chloroform, and carbon bisulphide, easily soluble in light petroleum, and insoluble in water, dilute acids, and alkalis. It forms a yellow solution in concentrated sulphuric acid which changes at once to red. Its solution in glacial acetic acid, on addition of sodium nitrite, turns red after a little time.

E. W. W.

Action of Acetic Acid and Zinc Dust on 2:5-Dimethylpyrroline. By CARLO U. ZANETTI and A. CIMATTI (*Ber.*, 1897, 30, 1588—1590).—When 2 : 5-dimethylpyrroline is reduced with zinc dust in acetic acid solution, the base, $C_{12}H_{17}N$, is obtained; it forms long, colourless needles melting at 74—75°, and becomes red on exposure to air. The *hydrochloride* and *picrate* melt at 242—244° and 200° respectively, and the *platinochloride* crystallises in yellow needles melting at 241—242°.

M. O. F.

Existence of Condensation Rings with Para-Linkage. By ALBERT LADENBURG (*Ber.*, 1897, 30, 1586—1588. Compare Harries, this vol., i, 293).—The constitution $N\begin{matrix}\diagup CHMe\cdot CH_2 \diagdown \\ -CS——NH- \\ \diagdown CMe_2—CH_2 \diagup\end{matrix}CH$ having been ascribed by Harries to α-amidotrimethylpiperidine eso-thiocarbamide (*loc. cit.*), the author points out that the properties of the substance are consistent with the formula $NH<\begin{matrix}CHMe\cdot CH_2 \\ CMe_2—CH_2\end{matrix}>CH\cdot N\colon CS$; he is of opinion that there is at present no ground for representing compounds as having para-linkage.

M. O. F.

Etherification of 2:3:4-Pyridinetricarboxylic Acid. By OTTO RINT (*Monatsh.*, 1897, 18, 223—243).—It is not possible to

obtain more than a diethylic salt, either by saturating an alcoholic solution of the acid with gaseous hydrogen chloride, or by acting on the acid with excess of phosphoric chloride and treating the product with alcohol; or by the action of sodium ethoxide and sodium ethylsulphate, or of phosphoric chloride and alcohol on the diethylic salt. The ethylic salt described by Dobbie and Ramsay (Trans., 1879, 189) and Roser (*Annalen*, 1886, **234**, 125) was in reality the diethylic salt. *Dimethylic* and *diethylic* 2 : 3 : 4-*pyridinetricarboxylates* [probably $COOH : (COOEt)_2 = 2 : 3 : 4$], are best prepared by saturating with gaseous hydrogen chloride a 10 per cent. solution of the acid in the absolute alcohol, and heating eventually to boiling; the *hydrochloride* of the salt separates out as the solution cools. The ethylic salt is the more easily prepared. The methylic and ethylic salts melt respectively at 165—166° and 118° (uncorr.); they are best prepared from the hydrochlorides, which melt at 177—178° and 142°, by boiling the latter with benzene in a current of carbonic anhydride until all the hydrogen chloride has been driven off. In the alcoholic mother liquor from the hydrochloride of the ethylic salt, diethylic cinchomeronate (3 : 4-pyridinedicarboxylate) was detected; the same substance is formed when diethylic pyridinetricarboxylate is heated for 24 hours at 150—160°, or for 6—7 hours with saturated alcoholic hydrochloric acid at 210° in a sealed tube, carbonic anhydride being evolved of course. When diethylic pyridinetricarboxylate is heated for 5 hours with ethylic iodide in a sealed tube at 110°, the iodide of ethylic ethylapophyllenate, $C_5H_3NEtI(COOEt)_2$ [$Et : I : (COOEt)_2 = 1 : 1 : 3 : 4$], (Blumenfeld, Abstr., 1896, i, 60) is formed. When it is allowed to remain for several days with aqueous ammonia saturated at $-10°$, it forms *ammonium pyridinetricarbodiamate*, $COONH_4 \cdot C_5(NH_2)\colon(CONH_2)_2$; this can be recrystallised from cold water, but on one occasion the *diammonium monomate*, $C_5NH_2(COONH_4)_2 \cdot CONH_2$, resulted from this process. These substances give *triammonium pyridinetricarboxylate*, $C_5NH_2(COONH_4)_3$, when boiled with water, and the first mentioned, when heated at 120—130° in a current of dry carbonic anhydride, yields the *amidimide*, $CONH_2 \cdot C_5NH_2 {<}{}^{CO}_{CO}{>} NH$. All of these substances decompose without melting when heated. C. F. B.

2 : 6-Diphenylpyridine and 2 : 6-Diphenylpiperidine. By Carl Paal and Karl Demeler (*Ber.*, 1897, **30**, 1499—1504).—After it had been shown that the 2 : 6-diphenylpyridine prepared from diphenacylmalonic and diphenacylacetic acids was identical with the compound obtained by Scholtz from the oxime of cinnamylideneacetophenone (Abstr., 1895, i, 562), attempts were made to convert it into some well-known derivative of pyridine, and with this object it was subjected to the action of concentrated nitric acid. Two isomeric dinitroderivatives were produced, namely, *α-dinitro*-2 : 6-*diphenylpyridine*, $C_5NH_3(C_6H_4 \cdot NO_2)_2$ [= 2 : 6], crystallising from glacial acetic acid in light yellow needles melting at 210—220°, and *β-dinitro*-2 : 6-*diphenylpyridine* crystallising from dilute alcohol in nodular masses melting at 110—111°.

On reducing the α-dinitro-compound with tin and hydrochloric acid,

the corresponding *a-diamido*-derivative is produced, which forms silky needles melting at 75—76°, and yields a *hydrochloride*, $C_{17}H_{15}N_3,3HCl$, crystallising in groups of needles, and decomposing at 300°; the platinochloride and aurochloride are unstable.

Dipicolinic acid [pyridine-2 : 6-dicarboxylic acid], $C_5NH_3(COOH)_2$, $[(COOH)_2 = 2 : 6]$, is formed when the free diamido-base is oxidised by potassium permanganate; it slowly separates from its aqueous solutions in white needles melting at 226—227°.

2 : 6-*Diphenylpiperidine*, $C_5NH_9Ph_2$, formed when diphenylpyridine is reduced in alcoholic solution with sodium, can be purified by recrystallising its hydrochloride. The base crystallises in colourless plates melting at 69°, the *hydrochloride* melts at 315—316°, the *platinochloride* at 206—207°, and the *aurochloride* at 202°. J. F. T.

Piperonylpicoline. By J. Thiemich (*Ber.*, 1897, **30**, 1578—1582). —*Piperonylpicoline*, $C_5NH_4 \cdot CH:CH \cdot C_6H_3:O_2CH_2$, is obtained by heating picoline with piperonaldehyde (1 mol.) and a small quantity of zinc chloride in a sealed tube at 190—200° during 6 hours; it melts at 109°, and separates from alcohol in small, lustrous crystals, which exhibit feeble blue fluorescence. The *hydrochloride* becomes brown at 260—261°, and melts at 265—267°, when it decomposes; the *picrate* forms dark yellow needles, sinters at 214°, and melts at 217°. The *platinochloride* melts and becomes black at 199—200°, the *aurochloride* is unstable, and the *mercurochloride*, which is yellow, becomes colourless in light, and melts at 239—240°; the *dibromide* is a white powder which readily decomposes.

Piperonylpipecoline, $C_5NH_9 \cdot CH_2 \cdot CH_2 \cdot C_6H_3:O_2CH_2$, is prepared by reducing the foregoing base with sodium and amylic alcohol; it is an odourless oil having alkaline action on litmus, and boils at 180—182° under a pressure of 100 mm. The *hydrochloride* crystallises in colourless, silky needles, and melts at 177°. The *picrate* and *platinochloride* melt at 178° and 189° respectively, and the *mercurochloride* is an oil which solidifies slowly. M. O. F.

2′-3′-Dimethylquinoline. By Ernst Fraenkel (*Chem. Centr.*, 1896, ii, 877; from *Diss. Freiburg*).—2′-3′-Dimethylquinoline, $C_9NH_5Me_2$, which melts at 67°, was prepared according to the description of Rhode and of Friedländer and Eliasberg with a view of investigating the bromination of a 3′-substituted quinoline and obtaining a 2′-3′quinolinedicarboxylic acid. The compound with methylic iodide which melts at 218°, after decomposition with potassium hydroxide, is converted into the methylic chloride compound by the action of hydrochloric acid. By allowing the products of the reaction to remain exposed to the air, or by oxidation with an alkaline solution of potassium ferricyanide, an alkylidene base, $C_9H_5Me_2N:CH_2$, is probably first formed from the quaternary base, $C_9H_5Me_2NMeOH$, originally produced, and then changes into 1′ : 2′ : 3′-*trimethyl*-4-*quinolone*, $C_9NH_4Me_3O$, which melts at 80°. Dyes are also produced. By oxidation of the dimethylquinoline with chromic acid, no dicarboxylic acid is formed, but only quinaldine-3-carboxylic acid which melts at 235—238°, whilst by oxidation with potassium permanganate only oxalic acid, carbonic anhydride, and ammonia are formed. Attempts

to brominate 2′-3′-dimethylquinoline directly failed; by nitration, however, a mononitro-compound results which melts at 95°, and is probably 4-nitro-2′-3′-dimethylquinoline. The amido-compound obtained from this by reduction forms salts with one equivalent of acid. The acetyl derivative melts at 190—195°, and the methylic iodide compound decomposes at 220°. On bromination, the amido-compound yields a dibromo-derivative, probably 1 : 3-dibromo-4-amido-2′-3′-dimethylquinoline, $C_9NH_2Me_2Br_2 \cdot NH_2$, which melts at 154°. From 2′ : 3′-dimethylquinoline two sulphonic acids can be prepared.

E. W. W.

Action of Ethylic Oxalate and Sodium Ethoxide on Quinaldine. By WILHELM WISLICENUS (*Ber.*, 1897, **30**, 1479—1480).—Dry sodium ethoxide (from 3·9 grams of sodium) and ethylic oxalate (28 grams) were dissolved in ether and then mixed with 25 grams of quinaldine. At the end of several weeks, the mixture had solidified to a dark red, gelatinous mass in which yellow crystals of *sodium quinaldineoxalate* [*quinolylpyruvic acid*] were embedded. When this salt was carefully acidified with sulphuric acid, the free acid, $C_9NH_6 \cdot CH_2 \cdot CO \cdot COOH$, was obtained as a yellow precipitate. After recrystallisation from water, it forms beautiful, red needles with a slight blue fluorescence, and decomposes above 170° without melting. It is readily soluble in hot water, its alcoholic solution gives a brownish-red coloration with ferric chloride, and it is partially decomposed into quinaldine and oxalic acid when boiled with alkalis (compare E. Erlenmeyer, jun., Abstr., 1889, 991).

J. J. S.

Derivatives of Piperazine. By W. HERZ (*Ber.*, 1897, **30**, 1584—1586).—When piperazine is heated with concentrated hydrochloric acid in sealed tubes at temperatures between 100° and 250°, no elimination of ammonia takes place; concentrated sulphuric acid also yields negative results, the sole product being piperazine *sulphate*, which is readily soluble in water. The *acetate* decomposes in air, and the *diacetyl* derivative crystallises in colourless plates, and melts at 134°. The carbon bisulphide *compound* sublimes at 212°, and is insoluble in ether, benzene, chloroform, and water; mercuric chloride and lead salts do not eliminate hydrogen sulphide, as in the case of certain products of condensation of amidopiperidine (this vol., i, 295).

Piperazine yields a colourless *compound*, $(C_4H_9N_2)_2CO,4HCl$, when heated with phosgene in sealed tubes at 50°; it dissolves readily in water, is sparingly soluble in other media, becomes brown at 200°, and blackens at 270°.

Benzaldehyde combines with piperazine, forming a *compound* which decomposes in the desiccator. The formaldehyde *compound*,

$$C_4H_{10}N_2,2CH_2O,$$

is colourless when dry, and becomes brown at 170°, finally sintering at 225°, when it blackens.

M. O. F.

Pyrimidines. By SIEGFRIED RUHEMANN and A. S. HEMMY (*Ber.*, 1897, **30**, 1488—1492. Compare this vol., i, 376).—An almost theoretical yield of ethylic phenylpyrimidonecarboxylate may be obtained when a similar method to that used for the preparation of ethylic pyroxoloncarboxylate (this vol., i, 445) is adopted.

Its *platinochloride*, $(C_{13}H_{12}N_2O_3)_2,H_2PtCl_6$, crystallises in yellowish-red prisms, which are decomposed by water. The *acid* obtained by the hydrolysis of the ethylic salt has both basic and acidic properties; it readily dissolves in concentrated hydrochloric acid, and is thrown down again on the addition of water.

Two ethylic ethoxyphenylpyrimidinecarboxylates are obtained by the action of ethylic iodide on the silver salt of the above-mentioned ethereal salt. The silver salt is most readily obtained by dissolving ethylic phenylpyrimidonecarboxylate in alcohol, and adding alcoholic solutions of ammonia and silver nitrate. The two ethylic salts are best separated by means of ether; the one which is present in much greater quantity, $CPh{<}{}^{N\cdot C(OEt)}_{-N:CH-}{>}C\cdot COOEt$, is readily soluble in ether, and crystallises from alcohol in colourless prisms melting at 58—59°. The amount of the second ethylic salt was too small for further investigation. When the ethylic salt melting at 58—59° is boiled with concentrated hydrochloric acid, it yields phenylpyrimidonecarboxylic acid; boiling alcoholic potash, on the other hand, yields a mixture of this acid with ethoxyphenylpyrimidinecarboxylic acid. These two acids are easily separated by means of absolute alcohol, which dissolves the ethoxyphenylpyrimidinecarboxylic acid with great readiness. This *acid*, $CPh{<}{}^{N\cdot C(OEt)}_{-N:CH-}{>}C\cdot COOH$, which is isomeric with ethylic phenylpyrimidinecarboxylate, crystallises in colourless needles, melts at 193—194°, and is readily soluble in alkalis or concentrated hydrochloric acid. Addition of silver nitrate to its ammoniacal solution precipitates a white, insoluble, and somewhat stable *silver* salt. The authors have attempted to prepare an alkylic derivative of ethylic phenylpyrimidonecarboxylate, in which the alkylic group should be attached to nitrogen, using a method similar to that employed by Fischer in the uric acid series (this vol., i, 267). On warming the ethylic salt with normal sodium hydroxide and methylic iodide, however, they found that the greater part of the ethylic salt was hydrolysed. A small quantity of a compound melting at 165° was obtained, but the quantity was too small to investigate.

When phenylpyrimidonecarboxylic acid is heated at 265°, it loses carbonic anhydride and yields *phenylpyrimidone*, $C_{10}H_8N_2O$, which distils at 260—263° under a pressure of about 30 mm. It crystallises from alcohol in glistening needles, melts at 207—208°, and is readily soluble in hot water and also in ammonia; from the latter solution, a *silver* salt, $C_{10}H_7AgN_2O$, may be obtained. Phenylpyrimidone also possesses basic properties, since it is soluble in concentrated hydrochloric acid and yields a *platinochloride*, $(C_{10}H_8N_2O)_2,H_2PtCl_6$, crystallising in yellowish-red prisms. J. J. S.

Formation of Pyrimidones. By C. WOLF (*Ber.*, 1897, 30, 1564—1565).—Although phenylhydrazine reacts with ethylic dicarboxyglutaconate, yielding alcohol, ethylic malonate, and ethylic phenylpyrazolonecarboxylate (Ruhemann and Morrell, Trans., 1892, 61, 794) benzamidoxime and ethylic dicarboxyglutaconate give rise

to ethylic phenylpyrimidonecarboxylate, $CPh\langle\begin{smallmatrix}N—CO\\NH\cdot CH\end{smallmatrix}\rangle C\cdot COOEt$ (Ruhemann, this vol., i, 376). M. O. F.

Action of Aluminium Chloride on the Chlorides of Carbodiphenylimide: Synthesis of Anilidoquinazolines. By HERBERT N. McCoy (*Ber.*, 1897, **30**, 1682—1693. Compare this vol., i, 422).—*2'-Anilido-3'-phenyl-4'-phenylimidodihydroquinazoline*, or *2' : 4'-diphenylimido-3'-phenyltetrahydroquinazoline*,

$$C_6H_4\langle\begin{matrix}N\!=\!\!=\!\!=\!C\cdot NHPh\\C(:NPh)\cdot NPh\end{matrix}, \text{ or } C_6H_4\langle\begin{matrix}NH——C:NPh\\C(:NPh)\cdot NPh\end{matrix},$$

is obtained by saturating a solution of carbodiphenylimide in benzene with hydrogen chloride, diluting the liquid with carbon bisulphide, and heating it in a reflux apparatus with aluminium chloride. It forms rhombic plates melting at 184°, and when heated with aniline at 110—160° yields an isomeric modification which crystallises in needles and melts at 171°; crystallisation from boiling alcohol also converts the compound melting at 184° into the isomeride.

2'-Anilido-3'-phenyl-4'-ketodihydroquinazoline, or *2-phenylimido-3'-phenyl-4'-ketotetrahydroquinazoline*, $C_6H_4\langle\begin{matrix}N\!=\!C\cdot NHPh\\CO\cdot NPh\end{matrix}$, or

$$C_6H_4\langle\begin{matrix}NH\cdot C:NPh\\CO—NPh\end{matrix},$$

is obtained by hydrolysing the foregoing compounds with alkalis, aniline being simultaneously produced; it crystallises from boiling alcohol in colourless needles, and melts at 163°. When further hydrolysed by concentrated hydrochloric acid in sealed tubes at 160—180°, it yields 3'-phenyl-2' : 4'-diketotetrahydroquinazoline, which melts at 272° (Paal, Abstr., 1894, i, 332, and Busch, Abstr., 1895, i, 307).

2'-Thio-3'-phenyl-4'-ketotetrahydroquinazoline, $C_6H_4\langle\begin{matrix}NH\cdot CS\\CO—NPh\end{matrix}$, is obtained by heating anthranilic acid with phenylthiocarbimide (1 mol.) and aqueous caustic soda (1 mol.), sufficient alcohol being added to yield a clear solution; orthophenylthioureidobenzoic acid is first formed, and then undergoes condensation. The thio-compound dissolves readily in alkalis, and is precipitated by carbonic anhydride, but is scarcely soluble in sodium carbonate; it crystallises from a mixture of alcohol and acetone in colourless, rectangular plates, and melts above 300° without decomposing. Oxidation with potassium permanganate converts the substance into 3'-phenyl-2' : 4-diketotetrahydroquinazoline. When heated with aniline in sealed tubes at 300°, it yields 2' : 4'-phenylimido-3'-phenyltetrahydroquinazoline.

2'-Ethylthio-3'-phenyl-4'-ketodihydroquinazoline, $C_6H_4\langle\begin{matrix}N\!=\!C\cdot SEt\\CO\cdot NPh\end{matrix}$, is prepared from the foregoing compound by the action of ethylic iodide in presence of alcoholic potash, and crystallises in colourless needles melting at 114°. Aniline at 300° converts it into 2'-phenylimido-3'-phenyl-4'-ketodihydroquinazoline.

2′-Chloro-3′-phenyl-4′-ketodihydroquinazoline, $C_6H_4<\begin{matrix}N{=}CCl\\ CO\cdot NPh\end{matrix}$, is obtained when chlorine is passed into a solution of thiophenylketotetrahydroquinazoline dissolved in chloroform, forming a colourless oil which crystallises; alkalis convert it into 3′-phenyl-2′ : 4′-diketotetrahydroquinazoline, and aniline gives rise to 2-anilido-3′-phenyl-4′-ketodihydroquinazoline.

2′-Anilido-3′-phenyl-4′-phenylimidodihydroquinazoline is produced when the foregoing chloro-compound is heated with phosphorus oxychloride and phosphorus pentachloride, and after removal of the former, treated with free aniline. M. O. F.

Conversion of Phenylphenazonium into Phenosafranine, and of Nietzki and Otto's Isorosinduline into Naphthophenosafranine. By FRIEDRICH KEHRMANN and W. SCHAPOSCHNIKOFF (*Ber.*, 1897, 30, 1565—1572).—When aqueous ammonia is added to the orange-yellow, alcoholic solution of acetylaposafranine chloride, and the liquid agitated during several hours, the colour changes to intense bluish-violet, and finally becomes magenta-red; the solution then contains monacetylphenosafranine, and on adding hydrochloric acid, heating the liquid, and evaporating, phenosafranine chloride crystallises. It is, therefore, possible to convert phenosafranine through aposafranine into phenazonium, and to regenerate phenosafranine from phenazonium through aposafranine and its acetyl derivative.

The acetyl derivative of isorosinduline chloride (compare Nietzki and Otto, Abstr., 1888, 843) is converted by ammonia into acetylnaphthophenosafranine chloride. Naphthophenosafranine chloride contains $1H_2O$, and forms a bluish-green solution in concentrated sulphuric acid; the platinochloride is red, and the nitrate crystallises in green needles. This change can only be explained on the assumption that acetylrosinduline and acetylisorosinduline have the formulæ,

$$NHAc\cdot C_{10}H_5<\begin{matrix}N\\ NPhCl\end{matrix}>C_6H_4, \text{ and } C_{10}H_6<\begin{matrix}N\\ NPhCl\end{matrix}>C_6H_3\cdot NHAc,$$

respectively.

The authors criticise the conclusions of Fischer and Hepp regarding the constitution of methylphenosafranine (this vol., i, 258). M. O. F.

Formation of Isoxazolines from Ketoaldehydes and Isonitrosoketones. By ROLAND SCHOLL (*Ber.*, 1897, 30, 1287—1292).—In the preparation of methylglyoxime from isonitrosoacetone and hydroxylamine hydrochloride, a compound of the formula $C_6H_9N_3O_3$ is obtained as a bye-product, and the formation of substances of this class seems to be general to this reaction. Similarly, compounds, characterised by containing the group N_3O_3 are formed when other isonitrosoketones react with hydroxylamine hydrochloride. The compound formed by the condensation of glyoxal with hydroxylamine hydrochloride can only be a derivative of isoxazoline, that is, 3-oximidomethyl-2-isoxazolonoxime, whilst of the two possible formulæ of the

compound $C_6H_9N_3O_3$, that of a 5-methyl-3-oximidoethyl-4-isoxazolon-oxime, $CMe\cdot(NOH)\cdot CH<\begin{matrix}C(NOH)\cdot CMe \\ \text{———}O\end{matrix}>N$, seems the more probable.

J. F. T.

5-Methyl-3-oximidoethyl-4-isoxazolonoxime. By ROLAND SCHOLL and MORITZ BAUMANN (*Ber.*, 1897, **30**, 1292—1313).—After the compound $C_6H_9N_3O_3$, obtained from isonitrosoacetone and hydroxylamine hydrochloride, had been identified as a 5-methyl-3-oximidoethyl-4-isoxazolonoxime, several derivatives of it were prepared, notably by the action of nitrogen tetroxide, nitrogen trioxide, and various strengths of nitric acid.

On treating the dioxime with a mixture of concentrated and fuming nitric acids, a substance is produced corresponding with the formula $C_6H_8N_2O_3$, and evidently formed by the elimination of an oxime group from the dioxime, since, on treatment with hydroxylamine hydrochloride, it again yields the dioxime $C_6H_9N_3O_3$; although this *monoximeketone*, $N<\begin{matrix}O\text{—}CHAc \\ CMe\cdot C{:}NOH\end{matrix}$, cannot be obtained in a pure condition, it readily forms a *hydrazone*, $C_{12}H_{14}N_4O_2$, crystallising from hot alcohol in yellow crystals melting at 208°.

By the action of nitrogen tetroxide on the dioxime suspended in ether, a *trioxime*, $C_6H_8N_4O_4$, evidently *5-methyl-3-dioximidoethyl-4-isoxazolonoxime*, $N<\begin{matrix}O\text{—}CH\cdot C(N\cdot OH)\cdot CH{:}NOH \\ CMe.C{:}N\cdot OH\end{matrix}$, is produced, which separates in slender, yellow needles containing 1 mol. H_2O, on pouring its solution in hot glacial acetic acid into water, and melts at 221°. By the further action of nitrogen tetroxide on this trioxime, a *substance*, $C_{12}H_{12}N_6O_7$, of unknown constitution is produced, together with a dioxime-ketone, $C_6H_7N_3O_4$; the former is obtained in the form of slender, snow-white needles, melting and decomposing at 267°, on pouring its solution in chloroform into ether, whilst the latter, which is evidently *3-oximidoacetyl-5-methyl-4-isoxazolonoxime*,

$$N<\begin{matrix}O\text{—}CH\cdot CO\cdot CH{:}N\cdot OH, \\ CMe\cdot C{:}N\cdot OH\end{matrix}$$

separates from hot water in the form of faintly yellow needles melting at 91°. The *sodium* salt forms slender, white needles, and the *silver* salt light yellow needles; hydroxylamine hydrochloride causes the reformation of the trioxime, $C_6H_8N_4O_4$; phenylhydrazine produces a yellow, crystalline *hydrazone*, $C_{12}H_{13}N_5O_3$, melting, with decomposition, at 234°; aniline, a *compound*, $C_{12}H_{14}N_4O_4$, separating from water in long, thick plates; dimethylparaphenylenediamine, a *compound*, $C_{14}H_{17}N_5O_3$, separating from hot alcohol in dark-red, metallic needles, melting, with decomposition, at 206°, and diazobenzene, a *compound*, $C_{12}H_{11}N_5O_4$, separating from hot benzene in dark-red needles, melting, with violent decomposition, at 208°.

The trioxime, $C_6H_8N_4O_4$, is converted, on careful treatment with "green" nitric acid, into a trioxime-ketone. *3-Oximidoacetyl-5-oximido-*

methyl-4-isoxazolonoxime, $N\!\!<\!\!\begin{array}{l}O\text{———————}CH\cdot CO\cdot CH\!:\!N\cdot OH\\ C(CH\!:\!N\cdot OH)\cdot C\!:\!N\cdot OH\end{array}$, which slowly separates from a mixture of chloroform and acetone in glistening, yellow prisms melting and decomposing at about 158°.

By the action of "green" nitric acid on the dioxime, $C_6H_9N_3O_3$, oxalic acid alone is produced. J. F. T.

Condensation Products of Methylisoxazolone with Aldehydes and Acetone. By ROBERT SCHIFF and M. BETTI (*Ber.*, 1897, **30**, 1337—1343).—It has been already shown (Abstr., 1896, i, 83, and Knoevenagel and Renner, *ibid.*, 189) that benzaldehyde condenses with the oxime of ethylic acetoacetate to form an isoxazolone of the type $CHR\!:\!C\!\!<\!\!\begin{array}{l}CMe\!:\!N\\ CO\text{—}O\end{array}$; the most convenient method of preparation is to mix 1 mol. each of a concentrated aqueous solution of hydroxylamine hydrochloride, ethylic acetoacetate, and aniline, and then add 1 mol. of the aldehyde, and a volume of 20 per cent. hydrochloric acid equal to the total volume, and warm on the water bath. The benzaldehyde compound is not so readily decomposed by alkalis as was thought; only half the aldehyde is eliminated, and a compound of the type $CHR\left(CH\!\!<\!\!\begin{array}{l}CMe\!:\!N\\ CO\text{—}O\end{array}\right)_2$, melting at 145°, remains after this aldehyde has been boiled off; if the mixture is acidified again, without being boiled, recombination takes place, and the isoxazolone is regenerated. Other aldehydes react in the same way, and so does a ketone, acetone, but ketonic acids do not, for ethylic acetoacetate gave the same compound as acetone gives. These isoxazolones, when in aqueous solution, must be regarded as existing in the form of acids,

$$COOH\cdot CHR\cdot CMe\!:\!NOH,$$

and these are more or less electrolytically dissociated. The acetone derivative, for example, is colourless; its solution in water is, however, yellow, and strongly acid in reaction; if sodium hydroxide is gradually added, the yellow colour deepens at first, reaches a maximum when 1 mol. of soda has been added, and then decreases until it disappears entirely. The action of diazobenzene chloride on the sodium salt of the acetone compound yields the phenylhydrazone of methylisoxazolone melting at 192° (compare Knorr and Reuter, Abstr., 1894, i, 372; melting point there given as 189°); nitrous acid yields a yellow substance melting and decomposing at 174°, probably the analogous *oxime*. The names and melting points of the new substances obtained are *metanitrobenzylidenemethylisoxazolone*, yellowish, 148—149°; *cinnamylidenemethylisoxazolone*, yellow, 175—176°; *piperonylidenemethylisoxazolone*, yellow, 220°; *salicylidenemethylisoxazolone*, yellow, 174—175°; *furfurylidenemethylisoxazolone* (acetic acid used instead of hydrochloric in its preparation), greenish-yellow, solution yellow to red with green fluorescence, 112—113°; *propylidenemethylisoxazolone*, 120—121°. C. F. B.

Isoxazolones. By LUDWIG CLAISEN (*Ber.*, 1887, **30**, 1480—1485. Compare Abstr., 1891, 468).—When ethylic ethoxymethylenemalonate (Abstr., 1895, i, 193) is heated with hydroxylamine, a substance

$C_6H_7NO_4$ is obtained to which the author assigns the constitution of *ethylic isoxazolone-β-carboxylate*, $O<\begin{matrix}N:CH \\ CO\cdot CH\cdot COOEt\end{matrix}$. It melts and decomposes at 160—165°, when slowly heated, but if quickly heated, at 183—185°; the compound has the properties of a strong acid and dissolves even in dilute solutions of alkali acetates, and is precipitated unaltered from these solutions on acidification. Ferric chloride gives a deep red coloration, copper acetate yields a bulky, green precipitate, and ammoniacal silver nitrate a white, crystalline precipitate. This *silver* derivative, when heated with methylic or ethylic iodide, yields alkyl derivatives to which the author attributes the following constitutions: $O<\begin{matrix}NMe\cdot CH \\ CO-C\cdot COOEt\end{matrix}$, m. p. 96—97°, $O<\begin{matrix}NEt\cdot CH \\ CO-C\cdot COOEt\end{matrix}$, m. p. 46°. Both are insoluble in dilute alkalis and give no coloration with ferric chloride. When boiled with alkalis, they are decomposed into alkali malonate and carbonate, methylamine or ethylamine being formed at the same time. The formation of the alkyl derivatives by the displacement of the double bond is similar to the reactions observed by Uhlenhuth in the case of the alkyl derivatives of phenyl- and methyl-isoxazolone (this vol., i, 444), and in the formation of antipyrine from phenylmethylpyrazolone and methylic iodide. The paper concludes with a criticism of Ruhemann's formula for isoxazolone (this vol., i, 445), and clearly shows that, although in the alkylic derivatives of isoxazolone the alkylic group is attached to nitrogen, yet it does not follow that an imido-group is present in the original isoxazolone, since the silver salts of numerous compounds, when heated with alkylic iodides, undergo intramolecular decomposition. J. J. S.

Diacetonalkamine. By M. KAHAN (*Ber.*, 1897, **30**, 1318—1326).—The diacetonalkamine for these experiments was prepared from diacetonamine oxalate by Heintz's method. On treatment with fuming hydrobromic acid, it gives the *hydrobromide of γ-bromohexylamine* (2-methyl-2-amino-4-brompentane), $NH_2\cdot CMe_2\cdot CH_2\cdot CHBrMe,HBr$, which, after recrystallisation from benzene, melts at 160—161°; it yields a *picrate* crystallising from water in yellow scales melting at 157°, the corresponding *hydrochloride of γ-chlorhexylamine*, when recrystallised from dilute alcohol, melts at 157°; *μ-phenyl-α-dimethyl-γ-methylpentoxazoline*, $N\ll\begin{matrix}CMe_2\cdot CH_2 \\ CPh\text{——}O\end{matrix}>CHMe$, prepared from γ-bromhexylamine hydrobromide and benzoic chloride, forms snow-white scales melting at 32°, and yields a yellow *picrate* melting at 162·5—164°, and a red *platinochloride*. By the action of thiobenzamide on the hydrobromide, *μ-phenyl-α-dimethyl-γ-methylpenthiazoline*,

$$N\ll\begin{matrix}CMe_2\cdot CH_2 \\ CPh\text{——}S\end{matrix}>CHMe,$$

is produced; this forms rhombic plates melting at 34°, and gives a *picrate* crystallising from alcohol in yellow, rhombic prisms melting at 152°, also a *platinochloride* decomposing at 223°; *μ-mercapto-α-dimethyl-γ-methylpenthiazoline*, $N\ll\begin{matrix}CMe_2\cdot CH_2 \\ C(SH)-S\end{matrix}>CHMe$, is formed when the hydrobromide reacts with carbon bisulphide in the presence of sodium

hydroxide; it crystallises from methylic alcohol in thick prisms melting at 180°. Its *methylic* salt, which is obtained as a strongly refractive, colourless oil of peculiar odour when the mercaptan is treated with sodium methoxide and methylic iodide in methylic alcohol solution, boils at 240° (761·5 mm.); the *picrate* of the methylic salt melts at 131° and the *platinochloride* decomposes at 190°.

Amidohexanesulphonic acid, $NH_2\cdot CMe_2\cdot CH_2\cdot CHMe\cdot SO_3H$, (2-methyl-2-amido-4-methyl-4-pentansulphonic acid) is formed by the oxidation of the above mercaptan, or, better still, its methylic salt, by means of chlorine; it does not melt below 310°.

Phenylhydroxyhexylthiocarbamide,

$$OH\cdot CHMe\cdot CH_2\cdot CMe_2\cdot NH\cdot CS\cdot NHPh,$$

prepared from diacetonalkamine and phenylthiocarbimide, separates from hot alcohol in snow-white crystals melting at 163—164°; on treatment with concentrated hydrochloric acid in a closed tube at 100°, it is converted into *N-phenylhexylen-ψ-thiocarbamide*,

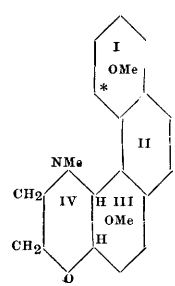
$$N{<}\begin{matrix}CMe_2\text{—}CH_2\\ C(NHPh)\cdot S\end{matrix}{>}CHMe,$$

which separates from dilute alcohol in crystals melting at 147—148°, and gives a *platinochloride* decomposing at 202°. With ethylthiocarbimide, diacetonalkamine yields *hydroxyhexylthiocarbamide*,

$$OH\cdot CHMe\cdot CH_2\cdot CMe_2,NH\cdot CS\cdot NHEt,$$

melting at 198·5°, and which with concentrated hydrochloric acid gives *N-ethylhexylene-ψ-thiocarbamide*, $N{<}\begin{matrix}CMe_2\text{—}CH_2\\ C(NHEt)\cdot S\end{matrix}{>}CHMe$, which, however, was not obtained in a crystalline condition; the *picrate* melts at 156—157°, and the *platinochloride* decomposes at 190—191°. J. F. T.

Thebaine. By MARTIN FREUND (*Ber.*, 1897, **30**, 1357—1393).—It will be convenient, for purposes of explanation, to give at once the formula that the author adopts for thebaine as a result of his investigations. The two methoxyl groups are in rings I and III respectively; that in I must be in one of the two positions indicated by an asterisk; that in III is very possibly at the lowest angle of the hexagon. In this abstract, the formula just given will be abbreviated to



Thebaine.

$$C_{14}H_8(OMe)_2{<}\begin{matrix}NMe\cdot CH_2\\ O\text{——}CH_2\end{matrix};$$

the left-hand part of this formula, corresponding with the right-hand part of the larger one, is to be regarded as a dihydrophenanthrene nucleus.

[With HUGO MICHAELS].—Thebenine,

$$OH\cdot C_{14}H_8(OMe){<}\begin{matrix}\text{—}CH\cdot NHMe\\ O\cdot CH_2\end{matrix},$$

is best obtained by dissolving 10 grams of thebaine at a time in a 100 c.c. of nearly boiling hydrochloric acid of sp. gr. 1·07, boiling for $1\frac{1}{2}$—2 minutes, cooling in ice and water, and recrystallising the hydrochloride, which separates, at first as a syrup, from hot water. The hydrochloride, with $3H_2O$, melts at 235°; the oxalate,

$$C_{18}H_{19}NO_3,C_2H_2O_4 + H_2O,$$

at 275—276° when heated quickly; the sulphate,

$$(C_{18}H_{19}NO_3)_2,H_2SO_4 + H_2O,$$

melts at 209—210°, and does not lose its water of crystallisation at 130—140°. Boiling with acetic anhydride converts thebenine into a substance which melts at 72—80° when crystallised from water, but when crystallised from absolute alcohol at 160—161°; it contains one methoxyl group, and cannot be reconverted by hydrolysis into thebenine; it is regarded as a *triacetyl* derivative,

$$OAc{\cdot}C_{14}H_6(OMe){\cdot}CH{<}{\begin{matrix}NAcMe\\CH_2{\cdot}OAc\end{matrix}}.$$

Thebenine, when boiled with phenylthiocarbimide in alcoholic solution, yields an amorphous *thiocarbamide*, $NHPh{\cdot}CS{\cdot}NC_{18}H_{18}O_3$, melting and decomposing at 85°. It also yields, with methylic iodide, thebeninemethinemethyliodide, $OH{\cdot}C_{14}H_8(OMe){<}{\begin{matrix}-CH{\cdot}NMe_3I\\O{\cdot}CH_2\end{matrix}}$, which melts at 206—208° when crystallised from alcohol, and decomposes into thebenol and trimethylamine when boiled with 30 per cent. aqueous soda; with ethylic iodide, thebenine yields an analogous compound, which decomposes into thebenol and methyldiethylamine. These reactions show that thebenine is a secondary base; were it a tertiary base, the amine obtained in the last case would have been dimethylethylamine. *Thebenol*, $OH{\cdot}C_{14}H_6(OMe){<}{\begin{matrix}CH_2\\-O-\end{matrix}}{>}CH_2$, melts at 186—188°; its *sodium hydrogen* salt, $C_{17}H_{13}NaO_3,C_{17}H_{14}O_3$, is completely melted at 210—212°. From 100 grams of thebaine, 60 of thebenine hydrochloride, 67 of the methinemethyliodide, and 33·5 of thebenol can be obtained. Thebenol gives an *acetyl* derivative melting at 102—103°, and a *methyl* derivative, melting at 133—134°. When boiled down with 30 per cent. aqueous potash until the water is nearly all driven off, it yields *northebenol*, $C_{14}H_6(OH)_2{<}{\begin{matrix}CH_2\\-O-\end{matrix}}{>}CH_2$, which melts at 202—203°; both this and thebenol itself, when boiled with strong hydriodic acid, give an *iodhydrin*, $C_{14}H_6(OH)_3{\cdot}CH_2{\cdot}CH_2I$, which is completely decomposed at 270°. Thebenol, further, is reduced to pyrene when it is distilled with zinc dust in a current of hydrogen, or when it is heated with strong hydriodic acid and phosphorus for 3—4 hours in a sealed tube at 220°.

[With Ernst Göbel].—When thebaine is boiled with acetic anhydride and anhydrous sodium acetate, it yields acetylthebaol and methylhydroxyethylamine, $NHMe{\cdot}CH_2{\cdot}CH_2{\cdot}OH$, the aurochloride of which melts at 145—147° (Knorr's substance, Abstr., 1889, 1218, was probably impure). The methiodide, under similar circumstances, yields acetylthebaol and dimethylhydroxyethylamine, the yellow aurochloride of which, $CH_{11}NO,HAuCl_4$, melts at 195°; but when it is boiled with aqueous potash, the amine evolved is *tetramethylethylenediamine*, $NMe_2{\cdot}CH_2{\cdot}CH_2{\cdot}NMe_2$, for it is identical with the product formed when dimethylamine (2 mols.) is heated with ethylenic bromide (1 mol.) for 3 hours at 100° in a sealed tube; the *hydrochloride*, with 2HCl of this base, decomposes at 300°; the *aurochloride*, with $2HAuCl_4$, at 205°; the *platinochloride*, with H_2PtCl_6, at 252°. *Acetylthebaol*, $C_{18}H_{16}O_4$, melts at 118—120°; with bromine in chloroform solution, it

gives a *dibromo*-substitution derivative, $C_{18}H_{14}Br_2O_4$, melting at 179°; and, when hydrolysed with alcoholic sodium ethoxide, it yields *thebaol*, $C_{14}H_7(OMe)_2\cdot OH$, which melts at 94°, and gives phenanthrene when distilled with zinc-dust in a current of hydrogen. Acetylthebaol is oxidised by chromic acid in acetic acid solution or by permanganate in cold dilute sulphuric acid to yellow *acetylthebaolquinone*, $C_{18}H_{14}O_6$, which melts at 203°, gives a red *bromo*-substitution derivative, $C_{18}H_{13}BrO_6$, melting at 310°, and is hydrolysed by alcoholic sodium ethoxide to yellow *thebaolquinone*, $C_{14}H_5O_2(OMe)_2\cdot OH$, which melts at 233°. These two quinones are hydroxydimethoxyphenanthrenequinones; they both condense with 3 : 4-tolylenediamine yielding dye-stuffs which are yellow in colour, but are turned purple-red by strong hydrochloric acid, and form a blue solution in strong sulphuric acid, and melt at 201—203° in the case of the acetyl derivative, at 192° in the other case. Thebaolquinone is oxidised by permanganate in the presence of cold dilute sulphuric acid to 1 : 2 : 3-methoxyphthalic acid, which melts at 138—144°, forming the anhydride, which then melts at 93—94° (Jacobsen, Abstr., 1883, 1124, gives 160° and 187°); this shows that the methoxyl group in the I ring of thebaine must be in one of the ortho-positions relatively to the II ring. When acetylthebaolquinone is oxidised with chromic acid in acetic acid solution, a smell of vanillin is always noticed when the product is being worked up; this makes it not unlikely that the methyl group in the III ring of thebaine may be in the ortho position relatively to the O atom of the IV ring. C. F. B.

Leuponic and Hexahydrocinchomeronic Acids. By WILHELM KOENIGS (*Ber.*, 1897, **30**, 1326—1332).—Hexahydrocinchomeronic acid, obtained by reducing monethylic cinchomeronate with sodium in boiling alcoholic solution (Abstr., 1896, i, 698), and melting at 237—238°, appears to be a mixture of the *cis*- and *trans*-modifications; heating with potassium hydroxide and a little water for 5—6 hours at 190—200° apparently converts it entirely into the more stable modification, for the acid, when regenerated after this treatment, melts and decomposes at 268—270° (or at 275° when heated quickly). It now crystallises in monoclinic tables, which were submitted to measurement; the very soluble *hydrochloride* and *hydrobromide* melt and decompose at 240—242° and 220—222° respectively, the *aurochloride* at 205°; the acid is optically inactive. Leuponic acid was obtained from the oxidation products of cinchonine (Skraup, this vol., i, 99); it is feebly dextrorotatory, and forms a colourless *nitrosamine* which melts and decomposes at 167—168°. When heated with potash and a little water, it is transformed into an acid identical in all respects with that described above. Leuponic acid must, then, be the unstable modification of cinchomeronic acid, and hence it must contain a pyridine ring. The author assigns to meroquinenine, cincholeuponic acid, and leuponic acid the constitution of hexahydropyridine (piperidine) derivatives, the 3 : 4 positions being occupied, in the respective cases, by the groups $CH\colon CH_2$ and $CH_2\cdot COOH$, COOH and $CH_2\cdot COOH$, and COOH and COOH. C. F. B.

Some Derivatives of Meroquinenine and Cincholeuponic Acid. By WILHELM KOENIGS (*Ber.*, 1897, **30**, 1332—1337).—Cincholeuponic

acid, when heated for 5 to 6 hours with potash and a little water (compare preceding abstract) is converted into an isomeric *acid*, $C_8H_{11}NO_4$, which is lævorotatory and melts and decomposes at about 246°; the *hydrochloride* and *nitrosamine* melt and decompose at 197° and 173—175° respectively.

1-*Ethylcincholeuponic acid*, $C_{10}H_{17}NO_4$, is obtained by treating diethylic cincholeuponate with ethylic iodide, and hydrolysing the product with dilute hydrochloric acid; it melts and decomposes at 214—215°. When boiled with acetic anhydride, it yields two isomeric substances, $C_{10}H_{15}NO_3$; the α-compound, formed in larger amount, melts at 194°, the β-isomeride at 105°. Both have the character of *anhydro-acids*; with silver carbonate, they yield *silver* salts, $C_{10}H_{14}NO_3Ag$, from which the anhydro-acids can be regenerated. The α-compound, when boiled with barium hydroxide, yields a *barium* salt, $(C_{10}H_{16}NO_4)_2Ba$, and the *acid* that can be liberated from this melts and decomposes at 228° (its *hydrochloride* at 180°) and is isomeric with the ethylcincholeuponic acid described above; when boiled with acetic anhydride, however, it gives the same mixture of α- and β-anhydro-acids.

When meroquinenine is heated with arsenic acid for 2 to 3 hours at 180—190°, hardly any oxidation takes place, but it is converted into a substance, $C_9H_{17}NO_3 + 2H_2O$, which melts at about 220° when anhydrous, its *hydrochloride* at 254—255°; to this substance is assigned provisionally the constitution of a *lactone*, the corresponding acid being the hexahydropyridine derivative, $[CH(OH)\cdot CH_3 : CH_2\cdot COOH = 3 : 4]$; an isomeric substance, the *hydrochloride* of which melts at 223—224°, is also formed in the reaction.

The *ethylic* salt of 1-*ethylmeroquinenine*, $C_{13}H_{23}NO_2$, is formed when the ethylic salt of meroquinenine is treated with ethylic iodide; its *hydrochloride* and *hydrobromide* melt at 165° and about 215° respectively. When the latter is brominated in chloroform solution, the compound $C_{13}H_{23}Br_2NO_2,HBr$, melting at about 182°, is formed, and this is converted by prolonged boiling with very dilute hydrobromic acid into a substance, $C_{11}H_{18}BrNO_2,HBr$, which melts at 218—220°.

C. F. B.

Constitution of Emetine. By HERMANN KUNZ-KRAUSE (*Chem. Centr.*, 1896, ii, 894; from *Schweiz. Woch. Pharm.*, **34**, 358. Compare Abstr., 1895, i, 118).—The author still regards the emetine he used as pure, in spite of Paul and Cownley's attempts to prove it a mixture of cephaeline and emetine. It has the formula $C_{30}H_{40}N_2O_5$, and contains four methoxy-groups. On oxidation with alkaline permanganate, it yields a yellow, amorphous substance, which, on further oxidation with nitric acid, forms a substance having a strong odour of sumbul root, and two acids containing nitrogen; the one gives a red coloration with ferrous sulphate, but the other does not react with it, and hence cannot be a 2-pyridinecarboxylic or 2′-quinolinecarboxylic acid. The latter acid, when heated with potassium, gives carbylamine, hence the author concludes that it, like emetine itself, does not contain a side chain united to nitrogen.

E. W. W.

Constitution of Pilocarpine. By PETER KUNDSEN (*Chem. Centr.*, 1896, ii, 708; from *Ber deutsch. Pharm. Ges.*, **6**, 164—172).—Accord-

ing to Hardy and Calmel, pilocarpine is a derivative of a β-substituted pyridine, since when oxidised it yields first pyridinetartronic acid and then nicotinic acid, and contains also a pentavalent nitrogen atom, since it may be synthesised from trimethylamine and pyridinelactic acid. The author does not place absolute confidence in these results, since no analyses are quoted, and only very insufficient details of the yields obtained in the various decompositions. He describes his own attempts to prepare pyridinelactic acid, to synthesise picolinelactic acid from aldehydecolidine (2 : 3-dimethylpyridine), and to obtain higher homologues of pilocarpine. E. W. W.

Eucaine. By GEORG MERLING (*Chem. Centr.*, 1896, ii, 709; from *Ber. deutsch. Pharm. Ges.*, **6**, 173—176).—Amygdalylmethyltriacetonealkamine, prepared from methyltriacetonealkamine, is, like tropine, a derivative of 4-hydroxymethylpiperidine, and to this the similarity of the physiological action of atropine, homatropine, and this alkamine is to be ascribed. Cocaine is a derivative of 4-hydroxypiperidinecarboxylic acid, and is closely related to atropine. The author describes experiments made to introduce benzoyl and methyl groups into the synthetically prepared 4-hydroxypiperidinecarboxylic acid, with a view to the preparation of anæsthetics which act locally. The synthesis of 3-hydroxypiperidinecarboxylic acid whose composition is analogous to that of ecgonine is also described. Eucaine, which is also obtained, and whose chloride is used in commerce as a substitute for cocaine, has the formula $NMe{<}\begin{matrix}CMe_2\cdot CH_2\\ CMe_2\cdot CH_2\end{matrix}{>}C{<}\begin{matrix}OBz\\ COOMe\end{matrix}$. E. W. W.

Iodine Reaction of Chitin. By ENOCH ZANDER (*Pflüger's Archiv*, 1897, **66**, 545—573).—For the iodine reaction of carbohydrates, water and some assisting substance must be present. The effect of various concentrated reagents on the colour reaction may be thus tabulated:

	Glycogen.	Soluble Starch.	Rice Starch.	Cellulose according to amount of iodine used.
Water	Weaker	Weaker	Weaker	Pale yellow to dark brown.
Zinc chloride, 70°/₀.	Disappears	Blue	Blue	
Zinc sulphate	Deeper	Violet	Brown	Colourless to dark violet.
Alum		Blue		—
Sodium acetate	Becomes violet	Red		—
Sodium chloride	Deeper	Deep blue		Yellow to dark brown.
Ammonium chloride		Blue		Yellow to dark brown.

In accordance with the relationship held to exist between chitin and carbohydrates, it is found that the iodine reaction it gives is almost identical with that given by glycogen. W. D. H.

Properties of Albumoses. By Fr. Kutscher (*Zeit. physiol. Chem.*, 1897, **23**, 115—120).—The research relates principally to deutero-albumose prepared from Witte's peptone. Its reactions are in the main those which have previously been described; some small points of difference in detail are noted. The principal new fact observed is that a solution of deutero-albumose, or of proto-albumose, or of Witte's peptone, causes a precipitate of serum-globulin, vitellin, myosin, or muscle-syntonin, when it is added to a solution of these substances in sodium carbonate. These products of digestion also precipitate nuclein from a neutral solution of nucleic acid in sodium carbonate Egg-albumin or serum-albumin is not precipitated. W. D. H.

Organic Chemistry.

Acetylene Solutions and their Explosive Properties. By MARCELLIN P. E. BERTHELOT and PAUL VIEILLE (*Compt. rend.*, 1897, **124**, 988—996, and 996—1000).—The authors have measured the pressures exerted at various temperatures between 3° and 75° by solutions of acetylene in acetone, the latter being saturated with the gas at 15° and under initial absolute pressures of about 7 kilos., 12 kilos., and 20·5 kilos. respectively. The volume of the gas dissolved per litre of acetone and per kilogram of absolute pressure varied in the three series from 23 to 24·6 volumes, and the volume dissolved increases proportionally with the pressure, as Claude and Hess have already observed. It is noteworthy that the pressures can be represented by Regnault's formula for the pressures of the saturated vapours of a large number of compounds, $\log F = a + b\alpha^t$, the constants for solutions of acetylene in acetone being $a = 5{\cdot}1134$, $b = 1{\cdot}5318$, and $\log \alpha = \bar{1}.99696$, a being very nearly the same as, and $\log \alpha$ being identical with, the corresponding value as given by Regnault for acetone alone. In all the series of experiments, the vapour pressure of the acetone was a very small proportion of the total pressure observed. It is very remarkable that the pressure of the gas in solution should follow the same general law as the pressures of the saturated vapours of homogeneous liquids, and that the value of $\log \alpha$ should be $\bar{1}.997$, which Regnault regarded as a constant common to all compounds.

Experiments were made to ascertain the effect (1) of a discharge of mercury fulminate, and (2) of an incandescent wire, on the solutions of acetylene in acetone. When the liquid has been saturated with the gas under an initial pressure not exceeding 13 kilos. at 15°, the explosion of the fulminate produces neither ignition nor explosion of the acetylene, and in this respect the solution of the gas resembles solutions of nitroglycerol in methylic alcohol. It will be seen later, however, that this ceases to be true under higher pressures.

When the acetone has been saturated with acetylene under a pressure not exceeding 10 kilos., the effect of an incandescent wire on the gas above the liquid is to cause the decomposition of the gas above the liquid, the pressure developed being the same as when pure acetylene is decomposed under the same pressure, but the decomposition does not extend to the gas that is dissolved in the liquid. When the wire is in the liquid, some of the dissolved gas is expelled by the rise of temperature, and this causes an elevation of pressure, but the decomposition is limited to the gas liberated from the liquid.

As the proportion of acetylene to acetone is increased by saturating the liquid with the gas under a higher pressure, the extent to which decomposition proceeds under the conditions specified is increased, and when saturation has taken place under pressures exceeding 20 kilos., an incandescent wire, either in the liquid or in the gas above it, brings about the decomposition of the whole of the acetylene with the production of pressures of several thousand atmospheres. At the same time,

the propagation of the explosive wave takes place with extreme slowness, and the decomposition in one case required 0·387 of a second. The development of pressure is at first very rapid, and afterwards much slower. The whole of the acetone is decomposed at the same time as the acetylene, the products being carbon, hydrogen, carbonic oxide, and carbonic anhydride.

Experiments made with large cylinders such as are used for holding compressed gases gave results similar to those obtained with the experimental tubes. No practicable receiver is capable of resisting the pressure developed by the complete decomposition of the acetylene and acetone.

In order to be within the limits of safety, it is important that the acetone should be saturated at pressures not exceeding 6 or 8 kilos., and that the cylinder be not exposed to such a rise of temperature as will bring the internal pressure up to a dangerous point. It is clear, however, that acetylene, when dissolved in a liquid like acetone, is much less dangerous than when pure, and a much larger quantity of the gas can be contained in a cylinder of a given size and yet remain within the limits of safety, when in the form of a solution, than when in the gaseous state. It is necessary, however, that the cylinders should be as strong as those generally used for containing liquefied carbonic anhydride. If from any cause the internal pressure approaches 20 kilos., the conditions become very dangerous.

An examination of the thermochemistry of the changes involved shows that the heat developed by the decomposition of the acetylene is not sufficient to compensate for the heat absorbed by the volatilisation and decomposition of the acetone, and at the same time to raise the temperature of all the substances concerned up to the point at which acetylene decomposes, except when the proportion of acetylene to acetone exceeds a certain limit, and this limit can only be reached under pressures which approach 20 kilos. At the same time, it is noteworthy that the decomposition of the acetone, notwithstanding the absorption of heat that it involves, greatly increases the pressure inside the vessel. The decomposition of the acetylene, resulting in the development of a large quantity of heat and a very high pressure, produces an instantaneous internal heating of the system similar to that produced by sudden compression, which, as Berthelot has shown, is capable of decomposing nitrous oxide.

The reaction described affords another example of the fact that a high pressure not only does not prevent the occurrence of exothermic reactions, but on the contrary assists them by increasing the velocity and lowering the limit of inflammability. C. H. B.

Propagation of Decomposition in Pure Acetylene Solutions. By MARCELLIN P. E. BERTHELOT and PAUL VIEILLE (*Compt. rend.*, 1897, **124**, 1000—1004).—Experiments were made with a view to ascertain, if possible, the exact conditions under which decomposition is not propagated through a mass of acetylene, whether initiated by an incandescent wire or by the explosion of a small quantity of fulminate. The former corresponds with local heating such as may be caused by friction or by the action of a small quantity of water on a large mass of carbide, the

latter corresponds with the explosion of small quantities of metallic acetylides such as might be formed by the contact of the acetylene with copper or its alloys in presence of ammonia or certain salts. Some experiments were made in vessels of from 4 to 25 litres capacity, with a diameter equal to their height; others were made in tubes 22 mm. in diameter and 3 metres long.

In the large vessels, with an incandescent wire, no inflammation of the gas took place under pressures not exceeding 520 mm. above normal pressure; there was inflammation in one case out of five with 610 mm. above normal, and in four cases out of seven with 700 above normal.

With mercury fulminate, there was no propagation of the decomposition when the pressure did not exceed 170 mm. above normal, but with 240 mm. above normal there was occasional propagation, and with higher pressures it became more frequent. These results are not materially influenced by the capacity of the vessel.

The experiments show that it is not possible to fix a limit below which propagation certainly will not take place and above which it certainly will take place. The probability of an explosion increases continuously with the pressure. For practical purposes, it would seem that there is very little danger of explosion by ignition when the pressure is not more than 520 mm. above normal, and of explosion by detonation when the pressure is not more than 170 mm. above normal.

In the experiments with the tube, there was no propagation of decomposition even with 0·1 gram of fulminate when the pressure did not exceed 760 mm. above atmospheric pressure. C. H. B.

Action of Acetylene on Silver Nitrate. By GEORGES ARTH (*Compt. rend.*, 1897, **124**, 1534—1536).—Silver acetylide is variously described as yellow and white. In reality, the precipitate formed on passing the gas through an ammoniacal solution of silver nitrate is at first yellow, but subsequently becomes colourless, even when excess of the hydrocarbon is employed. The compound $C_2Ag_2,AgNO_3$ (Keiser, Abstr., 1892, 1416) becomes deep yellow when treated with ammonia, but soon becomes colourless.

Silver acetylide, C_2Ag_2, is always produced when excess of acetylene is passed through an ammoniacal solution of silver nitrate, but the compound $C_2Ag_2,AgNO_3$ is formed in ordinary aqueous solutions, and is pure only when these are sufficiently concentrated. An N/2 solution of silver nitrate yields a colourless product, and the precipitate does not begin to be yellow until the dilution reaches N/24; the quantity of nitric acid set free increases with the dilution. It therefore appears that the initial action of acetylene on a neutral solution of silver nitrate gives rise to the compound $C_2Ag_2,AgNO_3$, which is converted into a yellow, intermediate compound of unknown composition, capable of existence in presence of ammonia, this substance ultimately yielding silver acetylide.

Silver acetylide and the compound $C_2Ag_2,AgNO_3$ dissolve readily in a solution of potassium cyanide, acetylene being regenerated.

M. O. F.

Preparation of Ether. By L. LÉON A. PRUNIER (*Compt. rend.*, 1897, **124**, 1239—1242).—The formation of sulphonic derivatives

during the preparation of ether (next abstract) indicates that the generally accepted explanation of the process is insufficient. It may be assumed that ethylic hydrogen sulphate, in contact with alcohol, forms diethylic sulphate, and the latter in contact with more alcohol yields ether, ethylic hydrogen sulphate being regenerated. Experiment shows that both ethylic hydrogen sulphate and diethylic sulphate yield sulphonic derivatives when heated between 100° and 140°, and it is noteworthy that the liberation of sulphurous anhydride and of ethylene in the action of sulphuric acid on alcohol begins at 130—140°. It may be assumed that, at 130—140°, ethylic hydrogen sulphate splits up into alcohol and sulphuric anhydride, and the latter, in presence of alcohol, forms isethionic acid, and subsequently its ethylic salt, $OH\cdot C_2H_4\cdot SO_2\cdot OEt$. The ethylic isethionate, in presence of alcohol, yields ether and isethionic acid, which is again converted into the ethylic salt, and so the cycle proceeds. At 140°, ethylic isethionate itself splits up into alcohol and sulphurous anhydride.

The behaviour of isethionic acid may be regarded as typical of that of other compounds of the same class. Ethylsulphonic acid, for example, by which it is most probably accompanied, would behave in a similar way. This view of the mode of production of ether is supported by the known process in which ether is obtained by the action of alcohol on benzenesulphonic acid, with intermediate formation of ethylic benzenesulphonate.

The limitation of the action is, in a large measure, due to the gradual removal of sulphuric acid from the sphere of activity, either in the form of sulphurous anhydride or by dilution by the water which is one of the products. C. H. B.

[Formation of Sulphonic Derivatives in the] Preparation of Ether. By L. Léon A. Prunier (*Compt. rend.*, 1897, **124**, 1028—1029). —Sulphonic derivatives exist in notable quantities in ordinary ether, from which they are readily removed by washing, but they exist in still larger quantities in the residues from the preparation of ether, and also in the liquids used for purifying it. They are produced by the action of moderately dilute sulphuric acid on ethylic hydrogen sulphate at 140°, and in the manufacture of ether they are produced in largest quantity when the temperature exceeds 140°, and especially when concentrated sulphuric acid is employed.

If the process is stopped when the liquid begins to turn black (165—175°), which is the point at which the liberation of ethylene begins, the liquid contains a large quantity of the sulphonic derivatives, which, after removal of sulphurous anhydride and decomposition of the ethylic hydrogen sulphate by boiling with water, can be separated in the form of barium salts in the usual way. C. H. B.

Action of Potash on Formaldehyde. By Marcel Delépine (*Compt. rend.*, 1897, **124**, 1454—1457).—When a concentrated solution of formaldehyde is diluted with water, development of heat occurs, but this phenomenon is followed by an absorption, which gradually reduces the temperature of the solution below the original point. Although the initial change may be followed quantitatively, and is found to be proportional in intensity to the degree of dilution, the absorption of heat is too gradual to admit of calorimetric determination.

Addition of a dilute or concentrated solution of formaldehyde to aqueous potash, on the other hand, causes immediate rise of temperature, unattended, however, with a secondary change. The numerical results, comformably with those obtained by Berthelot from acetaldehyde, show that the heat generated diminishes with dilution, but is augmented by excess of potash or of aldehyde, the latter displaying a more energetic influence than the alkali; also, that the energy of 3, 15, and 30 per cent. solutions of formaldehyde is the same, and that the energy regained during the heat absorption is equal to the heat lost on dilution.

Tollens and Grassmann observed that the freezing point of a freshly diluted formaldehyde solution is depressed to an increasing degree as time goes on, showing that such a solution does not attain a condition of equilibrium until a considerable period has elapsed. M. O. F.

Trioxymethylene and Paraformaldehyde. By MARCEL DELÉPINE (*Compt. rend.*, 1897, **124**, 1525—1528).—Determinations carried out with the calorimetric bomb gave the heat of combustion per gram-molecule (CH_2O), at constant pressure and volume, 122·9 Cal., the heat of formation of trioxymethylene, $C + H_2 + O = +40{\cdot}4$ Cal. If anhydrous trioxymethylene is boiled with water for many hours, it does not dissolve, it being necessary to heat the substances in sealed tubes at 130°; the aldehyde having the same heat of formation as trioxymethylene, its production from the latter is isothermic, but the formation of formic acid, methylic alcohol, and carbonic anhydride is decidedly exothermic.

A specimen of paraformaldehyde having the composition $(CH_2O)_8,H_2O$, gave the heat of combustion per gram-molecule (CH_2O), at constant pressure and volume, 120·8 Cal., whence the heat of formation amounts to $+42{\cdot}5$ Cal. Paraformaldehyde probably represents one of the terms of the dehydration series, $nCH_2(OH)_2 = (CH_2O)n,H_2O + (n-1)H_2O$, of which the fundamental, $CH_2(OH)_2$, and the first terms are dehydrated on concentration, the products, which are less readily soluble, being deposited from the solution, but never dehydrated; complete dehydration only occurs under the influence of such an agent as sulphuric acid. Thus the transformation of paraformaldehyde into trioxymethylene absorbs 2·1 Cal. M. O. F.

Action of Water on Formaldehyde as Related to the Rôle of this Substance in Plants. By MARCEL DELÉPINE (*Bull. Soc. Chim.*, 1897, [iii], **15**, 997—1002).—When trioxymethylene is heated with an equal weight of water at 200°, it yields carbonic anhydride, methylic alcohol, formic acid, and a small quantity of carbonic oxide, the last-named product being due to the action of heat on the solution of formic acid; the same result is effected at 130—140°. During this change, the oxygen in the tube is completely absorbed, although a cold solution of formaldehyde does not absorb the gas.

The author discusses the bearing which these results have on the question of the *rôle* played by formaldehyde in plants. M. O. F.

Magnesium Malonate. By GUSTAVE MASSOL (*Bull. Soc. Chim.*, 1896, [iii], **15**, 1103).—Magnesium oxide readily dissolves in solutions

of malonic acid at the ordinary temperature. Concentrated solutions yield the *salt* $C_3H_2O_4Mg + 4{\cdot}5H_2O$ in the form of large, transparent, monoclinic crystals. It loses part of its water when heated at 100°, yielding the *hydrate* $C_3H_2O_4Mg + 2H_2O$, which is also obtained during the evaporation of the aqueous solution between 90° and 100°. The complete dehydration takes place at 200—210°, and the anhydrous salt, when dissolved in water, evolves a considerable amount of heat.

$C_3H_4O_4$ sol. + MgO sol. = $C_3H_2O_4Mg$ sol. + H_2O sol. + 14·88 Cal.

J. J. S.

Zinc Malonate. By Gustave Massel (*Bull. Soc. Chim.*, 1896, [iii], **15**, 1104).—*Zinc malonate* crystallises as $C_3H_2O_4Zn + 2{\cdot}5H_2O$ in large, brilliant, monoclinic crystals sparingly soluble in water, the heat of solution, (212 grams in 4 litres) = − 1·48 Cal. When finely powdered and heated to 100°, it yields the compound $C_3H_2O_4Zn + H_2O$, which dissolves in water evolving + 4·79 Cal. The whole of the water is driven off at 150°, and the heat of solution of the anhydrous salt is + 5·65 Cal. Decomposition begins at 160°, and at higher temperatures the salt burns, leaving a residue of zinc oxide.

$C_3H_4O_4$ sol. + ZnO sol. = $C_3H_2O_4Zn$ sol. + H_2O sol. + 6·66 Cal.

J. J. S.

Racemic Transformation of Acid Ammonium Malate. By Frank B. Kenrick (*Ber.*, 1897, **30**, 1749—1757).—If the monosymmetric crystals of the acid ammonium malate are heated, a change occurs at about 70—75° into rhombic crystals resembling those of the active salt. The author has carried out experiments for the purpose of ascertaining whether the racemic modification does actually decompose into its two active components in accordance with the equation

$$2C_4H_5O_5{\cdot}NH_4,H_2O = (\overrightarrow{\ }C_4H_5O_5{\cdot}NH_4 + \overleftarrow{\ })C_4H_5O_5{\cdot}NH_4 + 2H_2O.$$

The presence of excess of one of the active components has no influence on the temperature of change of the racemic modification. Above a temperature of 80°, the active malate crystallises from a solution of the inactive salt, and solubility experiments carried out below the temperature of change also indicate that the transformation of the racemic modification takes place in accordance with the above equation.

H. C.

Preparation of Furfuran. By Paul Freundler (*Compt. rend.*, 1897, **124**, 1157—1159).—By the usual method of preparing furfuran, a very unsatisfactory yield of the substance is obtained. The author finds, however, that when pyromucic acid is heated in sealed tubes for 2 hours at 260—275°, a quantitative yield of furfuran is produced. When barium pyromucate is heated alone, the yield of furfurane exceeds the quantity of gases produced, but with increasing amounts of caustic soda, the yield of furfuran is diminished, and the quantity of gas, which is a mixture of carbonic oxide and a hydrocarbon, is very considerably increased. The *hydrocarbon*, C_3H_4, is ethylenic in character, and gives no precipitate with cuprous chloride or silver nitrate; the *tetrabromide*, $C_3H_4Br_4$, boils at 162° under a pressure of 20 mm., and rapidly undergoes decomposition at ordinary temperatures, yielding hydrogen bromide.

M. O. F.

Action of Chlorine on Orthamidophenols and Orthodiamines. By E. C. THEODOR ZINCKE (*Annalen*, 1897, **296**, 135—158. Compare Abstr., 1895, i, 131).—The author's previous investigations have shown that chlorine converts orthamidophenol and catechol into the orthodiketo-chloride, $C_6Cl_6O_2$, which is also produced by the action of the halogen on orthophenylenediamine. Physical considerations now confirm the formula $CCl{<}{}^{CCl\cdot CCl_2}_{CCl_2-CO}{>}CO$, originally proposed for this substance, but subsequently replaced by the expression $CCl_2{<}{}^{CCl:CCl}_{CCl_2-CO}{>}CO$. Alkali converts the diketo-chloride into hexachloropentenehydroxycarboxylic acid, $\begin{matrix}CCl\cdot CCl_2\\ \|\\ CCl\cdot CCl_2\end{matrix}{>}C(OH)\cdot COOH$, which melts at 111°, and passes into the isomeride (m. p. 186°), $\begin{matrix}CCl:CCl\\ |\\ CCl_2\cdot CCl_2\end{matrix}{>}C(OH)\cdot COOH$, when heated. Both acids yield perchlorindone, C_9Cl_6O, when heated with water, whilst oxidation with chromic acid converts them into the isomeric ketones, $\begin{matrix}CCl\cdot CCl_2\\ \|\\ CCl\cdot CCl_2\end{matrix}{>}CO$, and $\begin{matrix}CCl:CCl\\ |\\ CCl_2\cdot CCl_2\end{matrix}{>}CO$, which melt at 28° and 92° respectively, and give rise to a mixture of the two substances when heated; alkali converts the ketones into the acids $CCl_2{:}C{:}CCl\cdot CCl_2\cdot COOH$ (m. p. 127°), and $CCl_2{:}CCl\cdot CCl{:}CCl\cdot COOH$ (m. p. 97—98°) respectively, both these compounds yielding ethylidenepropionic acid on reduction with sodium amalgam.

This summary of previous work is followed by a discussion of the results described in the following abstracts. M. O. F.

Action of Chlorine on Orthamidoparacresol and Orthotolylenediamine, 1-Methylpentachloro-3 : 4-diketo-R-hexene, and its Products of Change. By E. C. THEODOR ZINCKE, F. BERGMANN, and BRUNO FRANCKE (*Annalen*, 1897, **296**, 159—179).—*1-Methylpentachloro-3 : 4-diketo-R-hexene hydrate*, $CClMe{<}{}^{CCl_2\cdot CO}_{CCl:CCl}{>}CO$, or $CMe{<}{}^{CCl_2\cdot CO}_{CCl\cdot CCl_2}{>}CO$, is produced when orthotolylenediamine hydrochloride is suspended in glacial acetic and concentrated hydrochloric acids, and submitted to the action of a current of chlorine; 1 : 3 : 4-amidocresol may also be employed as the source of this substance. The compound is very readily soluble in glacial acetic acid, alcohol, and ether, but dissolves with difficulty in benzene, from which it separates in colourless, prismatic, highly-refractive crystals, containing $2H_2O$; it melts at 90°, and becomes anhydrous in the desiccator, yielding a red oil which solidifies on exposure to moist air.

1 : 2 : 5 : 6-*Methyltrichlorocatechol*, $CMe{<}{}^{CCl\cdot C(OH)}_{CCl=CCl}{>}C\cdot OH$, is obtained by reducing a solution of the foregoing compound in glacial acetic acid with stannous chloride, and precipitating with concentrated

hydrochloric acid; it crystallises from dilute acetic acid in white needles containing the solvent, and melts at 179—180°. Chlorination regenerates methylpentachlorodiketohexene hydrate. The *acetyl* derivative crystallises from glacial acetic acid in small, colourless plates, and melts at 161°.

1 : 2 : 5 : 6-*Methyltrichlororthobenzoquinone*, $CMe{<}{\begin{matrix}CCl—CO\\CCl : CCl\end{matrix}}{>}CO$, is formed when methyltrichlorocatechol, mixed with a small quantity of glacial acetic acid, is cautiously added to a mixture of glacial acetic and nitric (sp. gr. 1·4) acids in equal quantities. It dissolves with great readiness in all solvents excepting water, and forms a deep red powder melting at 103°. Reducing agents convert the quinone into the catechol derivative, and chlorine regenerates methylpentachlorodiketohexene hydrate. Caustic soda develops a deep blue coloration, which becomes yellowish, and sodium carbonate forms a brownish-red solution; hydrochloric acid precipitates methyltrichlorocatechol from both solutions.

Methylpentachloro-R-*pentenehydroxycarboxylic acid* [Me : OH = 1 : 3] is obtained by adding small quantities of finely-powdered methylpentachlorodiketohexene hydrate to a well cooled 10 per cent. solution of sodium carbonate, maintained at 0° by the addition of ice; the use of too much alkali is to be avoided, as the decomposition is apt to proceed farther. The solution is decanted from undissolved substance into concentrated hydrochloric acid in which ice is suspended, the precipitate being dissolved in an ice-cold solution of sodium acetate, and quickly filtered into concentrated hydrochloric acid. It crystallises from benzene in snow-white needles, and melts at 99·5°; it contains $1H_2O$, which is not eliminated in the desiccator. The *acetyl* derivative crystallises from benzene in small, white needles, and melts at 161°.

1-*Methylpentachloro-3-keto*-R-*pentene*, $\begin{matrix}CCl\cdot CCl_2\\ \| \quad\quad\\ CMe\cdot CCl_2\end{matrix}{>}CO$, or

$$\begin{matrix}CCl=\!=\!=CCl\\ | \quad\quad\quad\\ CClMe\cdot CCl_2\end{matrix}{>}CO,$$

occurs in two modifications. The *a-ketone* is obtained by adding a 30 per cent. aqueous solution of chromic acid to a solution of the foregoing pentenehydroxycarboxylic acid dissolved in glacial acetic acid; it is a bright-yellow oil which has the sp. gr. = 1·608 at 15°, and boils at 160—165° under a pressure of 35 mm. Gaseous ammonia converts it into the *compound*, $NH_2\cdot C_5Cl_4MeO$, which crystallises from benzene in yellowish scales, and melts at 137°. The *β-ketone* is obtained by treating the original diketohexene derivative with excess of a hot solution of bleaching powder, and acidifying with hydrochloric acid; it forms large, monoclinic crystals, and melts at 92°. Gaseous ammonia has no action on the substance, which is converted by alcoholic ammonia into a dark, brownish-red oil; phenylhydrazine gives rise to the *compound* $C_5ClMe(N_2H_2Ph)_2O$, probably a pyrazolidone derivative, which crystallises from benzene in dark red needles or leaflets, and melts at 200°. *β-Methylpentachloro*-R-*pentene hydroxycyanide*, $OH\cdot C_5Cl_5Me\cdot CN$, is obtained by adding an alcoholic solution of potassium cyanide to a well-cooled solution of the ketone in absolute

alcohol; it crystallises in thick needles, and melts, evolving gas, at 110°.

a-Methyltetrachlorobutinenecarboxylic acid, $CCl_2:C:CMe\cdot CCl_2\cdot COOH$, or $CCl_2:CMe\cdot CCl:CCl\cdot COOH$, is obtained by agitating the α-ketone with a well cooled 5 per cent. solution of caustic soda, and then acidifying with hydrochloric acid; it separates from dilute acetic acid in compact, colourless crystals, and melts at 146°. The *methylic* salt is a colourless oil having a feeble odour.

a-Methylbutylenecarboxylic acid, $CHMe:CMe\cdot CH_2\cdot COOH$, or $CMe_2:CH\cdot CH_2\cdot COOH$, is prepared by reducing the foregoing acid with sodium amalgam. It is a colourless oil, having the characteristic odour of fatty acids, and boils at 205—207°; its sp. gr. = 0·9884 at 17°. The *dibromide* crystallises from light petroleum in four-sided prisms, and melts at 104—105°.

The *lactone* of methylhydroxyvaleric acid, $\begin{array}{l}CHMe\cdot CHMe\cdot CH_2\\ \vert\qquad\qquad\qquad\quad \vert\\ O\text{———————}CO\end{array}$, or $\begin{array}{l}CMe_2\cdot CH_2\cdot CH_2\\ \vert\qquad\qquad\quad \vert\\ O\text{—————}CO\end{array}$, is obtained from the incompletely reduced chlorinated acid by the action of hot, dilute sulphuric acid; it boils at 85° under a pressure of 20 mm., and at 205·5° under atmospheric pressure.

When methylpentachloropentenehydroxycarboxylic acid is treated with water or sodium acetate, the indifferent *compound* $C_{10}Cl_6Me_2O_2$ is produced, and this substance also occurs as a bye-product in the preparation of the acid from the diketo-chloride; it separates from glacial acetic acid in small, colourless crystals, and melts at 182°, undergoing decomposition. Phosphorus pentachloride at 150° converts it into the *compound*, $C_{10}Cl_8Me_2O$, which crystallises from hot, glacial acetic acid, and melts at 245—247° in closed tubes, subliming below this temperature.

The *acid* $C_5Cl_2MeO_2\cdot COOH$ is another bye-product, and crystallises from dilute alcohol in short, slender needles, melting indefinitely at 218°; the *barium* salt crystallises from hot water in needles, and the *methylic* salt forms nacreous needles melting at 94·5°. M. O. F.

Action of Chlorine on Trichlororthodiamidotoluene, 1-Methyl-2:3-diketopentachloro-R-hexene and its Products of Change. By E. C. THEODOR ZINCKE and WILHELM PRENNTZELL (*Annalen*, 1897, **296**, 180—198).—With certain modifications, the authors have adopted Seelig's method for the preparation of 1:2:3:4:5:6-diamidotrichlorotoluene from 1:4:5:6-trichlorotoluene, and of the latter from the hydrocarbon.

1-*Methyl*-2 : 3-*diketopentachloro*-R-*hexene hydrate*,

$$CCl_2<\begin{matrix}CCl=CCl\\ CMeCl\cdot CO\end{matrix}>CO,$$

is obtained by dissolving the diamine in glacial acetic and hydrochloric acids, saturating the liquid with hydrogen chloride, and then passing chlorine through the solution maintained at 5—10° until the dark colour changes to yellow; after some hours, the ammonium chloride is filtered off and the liquid evaporated at the ordinary temperature. The compound contains $2H_2O$, and melts at 86—88°.

1 : 4 : 5 : 6-*Methyltrichlorocatechol*, $C_6MeCl_3(OH)_2$, is prepared from the foregoing keto-chloride by reducing the solution in glacial acetic acid with stannous chloride; it crystallises in long, white needles, becomes brown at 160°, and melts at 168°. Ferric chloride develops a violet coloration with the hot, aqueous solution. The *acetyl* derivative crystallises in colourless leaflets and melts at 165°.

1 : 4 : 5 : 6-*Methyltrichlororthobenzoquinone*, $CMe{<}{\substack{CO-CO\\ CCl\cdot CCl}}{>}CCl$, is obtained by oxidising the catechol derivative with nitric acid; it dissolves with great readiness in organic solvents, and crystallises in dark red needles melting at 98°.

Methylpentachloro-R-*pentenehydroxycarboxylic acid*,

$$C_5MeCl_5(OH)\cdot COOH \quad [Me : OH = 1 : 2],$$

is produced when the finely powdered keto-chloride is added to a smaller quantity of 10 per cent. sodium carbonate solution than that required to dissolve it, the filtered liquid being immediately added to ice and hydrochloric acid. The oil which separates solidifies rapidly, and, when freshly crystallised, contains $1H_2O$ and melts at 90°; the lustrous, transparent scales become opaque in the desiccator, and the substance melts at 123°, evolving gas. The *acetyl* compound forms large, monoclinic prisms, and melts at 160°, evolving gas.

1-*Methylpentachloro-2-keto*-R-*pentene*, $\begin{matrix} CCl \equiv\!\equiv Cl \\ | \\ CCl_2\cdot CMeCl \end{matrix}{>}CO$, is obtained by the action of bleaching powder on the keto-chloride, and occurs in two modifications. The *a-ketone* is best prepared by oxidising the foregoing hydroxycarboxylic acid in glacial acetic acid with a 30 per cent. solution of chromic acid; it is a pale yellow oil of camphor-like odour, and is readily volatile in an atmosphere of steam. The substance boils at 155—156° under a pressure of 40—45 mm.; it has the sp. gr. = 1·610 at 19°, and the refractive index = 1·55127 at 21°. The *anilide* crystallises from alcohol in small, white needles, and melts at 195°; it becomes yellow when exposed to light, the colour being destroyed if the substance is kept in the dark. Alkali eliminates phenylcarbimide from the aniline derivative. Phenylhydrazine converts the α-ketone into the *compound* $C_{18}H_{15}N_4OCl$, which is probably a pyrazolidone derivative; it forms small, bright red needles, and melts at 202°. The *β-ketone* is obtained by agitating the keto-chloride with a solution of bleaching powder during several days, and acidifying the liquid with dilute hydrochloric acid; the mixture of ketones is distilled in a current of steam, and the liquid modification separated from the crystalline form by filtration. The β-ketone forms large, transparent crystals, and melts at 91°. Phenylhydrazine converts it into a compound melting at 197°, which is probably identical with the substance derived from the α-modification.

β-Methyltetrachlorobutinenecarboxylic acid,

$$CMeCl{:}CCl\cdot CCl{:}CCl\cdot COOH,$$

is prepared by adding the keto-chloride to a 10 per cent. solution of caustic soda with continual agitation, and filtering the liquid into hydrochloric acid; it crystallises from benzene in transparent prisms, and separates from dilute acetic acid in beautiful, white needles

melting at 145°. The *sodium* and *potassium* salts dissolve readily in water, and the *ammonium* salt melts at 170°, evolving gas and becoming red; the *silver* salt crystallises from alcohol in small, white needles, the *barium* salt contains $5H_2O$, and the *methylic* salt is a colourless liquid.

β-Methylbutylenecarboxylic acid, $CH_2Me\cdot CH\colon CH\cdot CH_2\cdot COOH$, arises from the foregoing substance on reduction with sodium amalgam, and forms a colourless oil which boils at 120—123° under a pressure of 28 mm., and at 203—204° under atmospheric pressure. The *calcium* salt contains $3H_2O$, and the *silver* salt crystallises from water, but is in part reduced during the operation.

As in the case of α-methyltetrachlorobutinenecarboxylic acid (foregoing abstract), an indifferent *compound*, $C_{10}Cl_6Me_2O_2$, is produced when the keto-chloride is treated with caustic soda; it crystallises in small, colourless needles, and melts at 175°, evolving gas. The substance is also obtained by reducing the α-ketone with stannous chloride. M. O. F.

Action of Chlorine on Metamido-orthohydroxymetaxylene and Orthodiamidometaxylene, 1 : 3-Dimethyl-4 : 5-diketotetrachloro-R-hexene and its Products of Change. By E. C. THEODOR ZINCKE and BRUNO FRANCKE (*Annalen*, 1897, **296**, 198—216).—1 : 3-*Dimethyl*-4 : 5-*diketotetrachloro*-R-*hexene hydrate*,

$$CMe{<}{\substack{CCl_2\cdot CMeCl\\ CCl\text{———}CO}}{>}CO, \text{ or } CMeCl{<}{\substack{CCl\colon CMe\\ CCl_2\text{—}CO}}{>}CO,$$

is prepared by suspending orthodiamidometaxylene hydrochloride in glacial acetic and concentrated hydrochloric acids and saturating the liquid with chlorine, the colour of the solution finally becoming yellow; the ammonium chloride is removed by filtration, and the acetic acid allowed to evaporate at the ordinary temperature. The substance crystallises in colourless, monoclinic prisms containing $2H_2O$, and melts at 63°; at 64°, it becomes opaque and solidifies, but on cooling below 64°, it again becomes transparent and liquid; a second fusion occurs at about 130°, the substance beginning to boil at 196°, when it becomes brown. The *methoxide*, $OH\cdot C_6Me_2Cl_4O\cdot OMe$, is obtained by boiling a solution of the hydrate in methylic alcohol in a reflux apparatus, and pouring the concentrated liquid into water; it crystallises in transparent, monoclinic prisms, sinters at 100°, and melts at 118—120°. The hydrate may also be prepared from *metamido-orthohydroxymetaxylene*, which crystallises from alcohol in brownish, nacreous leaflets, and melts at 133—134°.

1 : 3-*Dimethyl*-2 : 6-*dichlorocatechol*, $CMe{<}{\substack{CCl\text{—}CMe\\ CCl\colon C(OH)}}{>}C\cdot OH$, is prepared by reducing the keto-chloride dissolved in glacial acetic acid with stannous chloride; it melts indefinitely at 149°, and sublimes if heated for some time at 110—120°. The *acetyl* derivative crystallises from glacial acetic acid, and melts at 161°.

1 : 3-*Dimethyl*-2 : 6-*dichlororthoquinone*, $CMe{<}{\substack{CCl\colon CMe\\ CCl\text{—}CO}}{>}CO$, is obtained by oxidising the catechol derivative with nitric acid; it forms a dark red, crystalline powder, and melts at 108°.

Dimethyltetrachloroketo-R-*pentene*, $\begin{matrix}CMe{=\!=}CCl\\ |\\ CCl_2\cdot CMeCl\end{matrix}\!\!>\!CO$, or

$\begin{matrix}CMeCl\cdot CCl_2\\ |\\ CCl{=\!=}CMe\end{matrix}\!\!>\!CO$,

is obtained by the action of bleaching powder on the diketo-chloride, and occurs in two modifications. The *α-ketone* is liquid, and may be filtered from the solid modification; this crystallises from the oil after distillation in a current of steam, and boils at 135° under a pressure of 30 mm., but has not yet been obtained unmixed with the isomeride. The *β-ketone* separates from benzene in large, monoclinic crystals, and melts at 60°; it has a pungent odour suggestive of camphor, and is readily volatile at the ordinary temperature.

Dimethyltrichlorobutinenecarboxylic acid,
$CMeCl\!:\!CCl\cdot CMe\!:\!CCl\cdot COOH$,
or $CCl_2\!:\!CMe\cdot CCl\!:\!CMe\cdot COOH$, is prepared by dissolving the α-ketone in 10 per cent. caustic soda, and acidifying with hydrochloric acid; it crystallises from benzene in beautiful, rhombic plates, and melts at 112°.

Dimethylbutylenecarboxylic acid, $CH_2Me\cdot CH\!:\!CHMe\cdot CH_2\cdot COOH$, or $CMe_2\!:\!CH\cdot CHMe\cdot COOH$, is obtained from the foregoing compound by reduction with sodium amalgam; the *silver* salt is amorphous. When heated with water, it yields a *lactone*, which separates from light petroleum in monoclinic crystals and melts at 47—48°.

The indifferent *compound*, $C_{10}Cl_4Me_4O_2$, is obtained by the action of caustic soda on the keto-chloride (compare foregoing abstracts); it separates from its solutions in large, monoclinic crystals, and melts at 173°. The substance is very indifferent towards alkalis, bases, and oxidising agents. The *acid*, $C_5ClMe_2O_2\cdot COOH$, is another bye-product of the action of caustic soda on the keto-chloride, and crystallises from water or glacial acetic acid in small, white needles melting at 185°; the *silver* salt is a white, crystalline powder, and the *ammonium* salt forms white leaflets. The *methylic* salt crystallises from benzene and melts at 81·5°.

M. O. F.

Action of Chlorine on Orthodiamido-ψ-cumene. By E. C. THEODOR ZINCKE and FRANZ HODES (*Annalen*, 1897, **296**, 216—219).—When chlorine acts on orthodiamido-ψ-cumene hydrochloride suspended in glacial acetic and hydrochloric acids, ammonium chloride separates, and the liquid becomes brown; no crystalline product has been obtained from the filtrate, but reduction of the oil obtained after evaporating the solvent gives rise to a derivative of catechol (compare foregoing abstracts).

1 : 4 : 5 : 6-*Trimethylchlorocatechol*, $CMe\!<\!\begin{matrix}C(OH)\cdot C(OH)\\ CCl{=\!=}CMe\end{matrix}\!>\!CMe$, is obtained by dissolving the oil in glacial acetic acid and reducing the solution with stannous chloride and hydrochloric acid; it crystallises from dilute alcohol or dilute hydrochloric acid, and melts at 131—132°. The *acetyl* derivative crystallises from glacial acetic acid in lustrous, colourless leaflets, and melts at 162—163°.

1 : 4 : 5 : 6-*Trimethylchlororthoquinone*, $CMe\!<\!\begin{matrix}CO-CO\\ CCl\cdot CMe\end{matrix}\!>\!CMe$, is pre-

pared by oxidising the catechol derivative with nitric acid; it separates from benzene in small, dark-red crystals, and melts at 96—97°.

M. O. F.

Hydrogenation of Orcinol. By DANIEL VORLÄNDER and FRITZ KALKOW (*Ber.*, 1897, **30**, 1801—1803).—When orcinol is heated with a solution of sodium hydrogen carbonate and sodium amalgam in a reflux apparatus while carbonic anhydride is passed through the liquid, metamethyldihydroresorcinol is produced (compare Knoevenagel, Abstr., 1896, i, 289). Methyldihydroresorcinol undergoes hydrolysis as in the case of dihydroresorcinol (this vol., i, 272); dimethyldihydroresorcinol (this vol., i, 276), however, resists the action of barium hydroxide in sealed tubes at 150—160°.

Methyldihydroresorcinol *dioxime* crystallises from boiling water in lustrous prisms, and melts at 155—157°. The formaldehyde *compound*, $C_{15}H_{20}O_4$, crystallises from hot alcohol in white needles, melts at 152°, and develops a brown coloration with ferric chloride; it probably has the constitution $CHMe{<}{\substack{CH_2\cdot CO\\ CH_2\cdot CO}}{>}CH\cdot CH_2\cdot C{<}{\substack{C(OH)\cdot CH_2\\ CO\text{——}CH_2}}{>}CHMe$, as its behaviour towards alkalis resembles that of a monobasic acid.

Methylenebisdihydroresorcinol is converted by dehydrating agents into the *anhydride*, $\begin{matrix} CH_2\cdot CH_2\cdot C\text{—}O\text{—}C\cdot CH_2\cdot CH_2 \\ CH_2\text{—}CO\cdot C\cdot CH_2\cdot C\cdot CO\text{—}CH_2 \end{matrix}$, which melts at 165°, and regenerates the methylene compound when heated with water in a sealed tube. Alcoholic ammonia converts methylenebisdihydroresorcinol into the acridine *compound*,

$$\begin{matrix} CH_2\cdot CH_2\cdot C\text{—}NH\cdot C\cdot CH_2\cdot CH_2 \\ CH_2\text{—}CO\cdot C\cdot CH_2\cdot C\cdot CO\text{—}CH_2 \end{matrix},$$

a yellow substance which melts and decomposes above 300°, and exhibits green fluorescence in solution; this derivative is also obtained by the action of ammonia on the foregoing anhydride, and yields acridine when distilled with zinc dust.

Boiling caustic alkali converts methylenebisdihydroresorcinol into the dibasic ketonic *acid*, $\begin{matrix} CH_2\cdot CH_2\cdot C\cdot CH_2\cdot CH_2\cdot CH_2\cdot COOH \\ CH_2\cdot CO\cdot C\cdot CH_2\cdot CH_2\cdot COOH \end{matrix}$, which melts at 76°. The tetramethyl derivative, however, resists the action of alkali.

M. O. F.

Purification of Hydrocarbons from Thiophen, its Homologues, and other Impurities by means of Aluminium Chloride. Application to the Purification of Benzene and Toluene. By ALBIN HALLER and EDMOND MICHEL (*Bull. Soc. Chim.*, 1897, [iii], **15**, 1065—1070. Compare Heusler, Abstr., 1895, i, 258).—Precipitation of thiophen with mercuric sulphate (Denigès, Abstr., 1895, ii, 372), is not applicable to purification of large quantities of benzene; aluminium chloride, however, may be used advantageously for this purpose.

The hydrocarbon is agitated with aluminium chloride, which develops a red coloration, and causes the deposition of a viscous liquid; after some time, the hydrocarbon is decanted from this product, and submitted to distillation, water, in any form, being carefully excluded.

The amount of aluminium chloride employed depends on the degree of purity of the benzene; a specimen which has already undergone treatment with sulphuric acid requires about 1 per cent., as much as 5 per cent. being used for the crude hydrocarbon boiling at 80—81°.

This process is applicable to toluene, but the results are less satisfactory. M. O. F.

Tertiary Parabutyltoluene and its Nitro-derivatives. By M. BIALOBRZESKI (*Ber.*, 1897, **30**, 1773—1776).—The action of aluminium chloride on a mixture of toluene and butylic haloid gives rise to tertiary butyltoluene, alike whether the tertiary or iso-alkylic derivative is employed (Baur, Abstr., 1894, i, 446), and the author finds that ferric chloride effects the same result, involving rearrangement and conversion of the isobutylic into the tertiary butylic radicle. Whilst, however, the hydrocarbon obtained by Baur yields metabutylbenzoic and isophthalic acids on oxidation, and is therefore metabutyltoluene, the product of the action of ferric chloride is converted into parabutylbenzoic and terephthalic acids on oxidation, and must be therefore regarded as the para-derivative.

Tertiary parabutyltoluene, $C_6H_4Me{\cdot}C_4H_9$, boils at 189—190° under a pressure of 758 mm., and has the sp. gr. = 0·8784 and 0·8611 at 0° and 23° respectively. The *dinitro*-derivative crystallises from dilute alcohol, and melts at 94—95°; it has a feeble odour of musk. M. O. F.

Trihydroxyphenylenic Bisulphide. By P. GENVRESSE (*Bull. Soc. Chim.*, 1897, [iii], **15**, 1038—1048. Compare this vol., i, 240).—The author is disposed to regard thianthrene (Kraft and Lyons, Abstr., 1896, i, 297) as having the sulphur atoms in the meta-position, Zorn and Brunel (Abstr., 1895, i, 287) having shown that in aromatic sulphones the group SO_2 is in the meta-position; moreover, hexamethyldiphenylene bisulphide may be prepared from mesitylene in presence of excess of the hydrocarbon.

Hexamethyldiphenylene bisulphide, $C_6HMe_3{:}(S)_2{:}C_6HMe_3$, is prepared by heating mesitylene with sulphur and aluminium chloride during 6 hours. It boils, and in part decomposes, at 275° under a pressure of 15 mm.; it is a viscous liquid, and gives a red coloration with concentrated sulphuric acid.

Hexamethyldiphenylene disulphone, $C_6HMe_3{:}(SO_2)_2{:}C_6HMe_3$, is obtained by oxidising the bisulphide with chromic acid in glacial acetic acid, and forms yellowish-white crystals; it decomposes above 300° without undergoing fusion.

The phenolic character of trihydroxyphenylenic bisulphide has been already indicated (this vol., i, 240). The *mono-silver* derivative separates from the aqueous solution in reddish-black crystals. The phthalic anhydride *compound*, $C_{20}H_8S_4O_7$, is obtained by heating trihydroxydiphenylenic bisulphide with phthalic anhydride in sealed tubes at 200° during 10 hours; it is an amorphous substance, dissolves readily in alkalis, and melts at 185°. The alcoholic solution dyes cotton pale red. M. O. F.

Phthalyl and Succinyl Ethers of Eugenol. By M. ROGOFF (*Ber.*, 1897, **30**, 1795—1796).—The *succinyl* derivative of eugenol is

obtained by heating eugenol with succinic chloride during 4 hours on the water bath, and crystallising the product from glacial acetic acid; it melts at 89·5—90°; aniline forms succinanilide when heated with the substance on the water bath, and phenylhydrazine gives rise to the succinyl derivative. The *phthalyl* derivative of eugenol crystallises in needles, and melts at 98·5—99°; phthalanil is formed under the influence of aniline, but phenylhydrazine has no action on the substance. M. O. F.

Mixed Amidines. By HANS VON PECHMANN (*Ber.*, 1897, **30**, 1779—1783. Compare Abstr., 1896, i, 31; also the following abstract).—The outcome of previous work on mixed amidines indicates that compounds of the general formulæ, NX:CR·NHY and NHX·CR:NY, independently of the method of their preparation, occur in one form only, but when X and Y represent chemically similar substituents, this form exhibits tautomerism, inasmuch as methylation gives rise simultaneously to the compounds NX:CR·NMeY and NMeX·CR:NY; in the case of dissimilar substituents, one alkylic derivative only is produced, the alkylic group becoming attached to the nitrogen atom, with which is combined the substituent of higher molecular weight, and thus establishing the constitution of the original amidine. An exception to the latter generalisation, however, is afforded by phenylbenzylamidine (following abstract), which has the constitution NHPh·CPh:N·CH_2Ph.

Phenylbenzenylamidine, NH:CPh·NHPh, was first obtained by Bernthsen, who ascribed to it the foregoing constitution, a conclusion which has been also confirmed by Lottermoser (this vol., i, 38); although treatment of benzanilideimidochloride with ammonia might be expected to yield the isomeric substance NH_2·CPh:NPh, the action in question affords a convenient method of preparing the base. It crystallises from alcohol, and melts at 112°, the hydriodide melting at 169—170°.

Phenylbenzenylmethylamidine, NH:CPh·NMePh, is obtained by the action of methylic iodide at the ordinary temperature; it crystallises from petroleum in colourless, prismatic needles, and melts at 85°. The *hydriodide* and *picrate* melt at 214° and 184° respectively. When heated with methylic iodide, phenylbenzenylamidine yields methylphenylamidobenzenylmethylimidine, which melts at 56° (Abstr., 1896, i, 32).

Hydrolysis with boiling acids or a 20 per cent. solution of caustic soda resolves phenylbenzenylmethylamidimidine into methylaniline, ammonia, and benzoic acid.

The author considers that the recognition of labile modifications of certain mixed diazoamido-compounds, recently described by Hantzsch and F. M. Perkin, has no very secure foundation. M. O. F.

Mixed Amidines. By HANS VON PECHMANN and BERTHOLD HEINZE (*Ber.*, 1897, **30**, 1783—1789. Compare foregoing abstract). —*β-Naphthylphenylbenzenylamidine*, NPh:CPh·NH·$C_{10}H_7$, or

NHPh·CPh:N·$C_{10}H_7$,

produced alike from benzanilide imidochloride and β-naphthylamine,

or benzonaphthalide imidochloride, crystallises from dilute alcohol in bright yellow prisms melting at 147°. When heated with methylic iodide for 10 hours at 90—100° in closed vessels, it yields a mixture of *benzenylmethylphenylamido-β-naphthylimidine*, $NMePh\cdot CPh\colon N\cdot C_{10}H_7$, which is obtained from β-benzonaphthalide imidochloride and methylaniline, and melts at 84°, and *benzenylmethyl-β-naphthylamidophenylimidine*, $NPh\colon CPh\cdot NMe\cdot C_{10}H_7$, prepared from benzanilide imidochloride and β-methylnaphthylamine, which melts at 110°; the *hydriodides* of the methyl bases melt at 243° and 230·5° respectively, whilst the mixture of bases obtained on methylating the original amidine melts at 78°, and yields a mixture of hydriodides which melts at 218°. β-Methylnaphthylamine is prepared by heating equal parts of β-naphthylamine and methylic iodide with two parts of wood spirit in sealed tubes for 12 hours at 100°; when regenerated from the nitrosamine, it is a colourless oil which boils at 296° under a pressure of 715 mm. The nitrosamine forms nacreous scales, and melts at 90°.

Metanitrodiphenylbenzenylamidine, $NPh\colon CPh\cdot NH\cdot C_6H_4\cdot NO_2$, or $NHPh\cdot CPh\colon N\cdot C_6H_4\cdot NO_2$, is prepared from benzanilide imidochloride and metanitraniline, as also from benzometanitranilide imidochloride and aniline; it crystallises in lemon-yellow prisms, and melts at 118°. Methylation converts it into a mixture of *benzenylmethylphenylamidometanitrophenylimidine*, $NMePh\cdot CPh\colon N\cdot C_6H_4\cdot NO_2$, obtained from benzonitranilide imidochloride and methylaniline, melting at 107·5°, and *benzenylmethylmetanitrophenylamidophenylimidine*,

$$NPh\colon CPh\cdot NMe\cdot C_6H_4\cdot NO_2,$$

which is prepared from benzanilide imidochloride and metanitromethylaniline, and melts at 97·5°; the *hydriodides* of these bases melt at 235° and 242° respectively, whilst the mixture of bases obtained on methylating the original amidine melts at 84°, and yields the mixture of hydriodides melting at 224°. *Benzometanitranilide imidochloride*, $CPhCl\colon N\cdot C_6H_4\cdot NO_2$, crystallises from benzene in colourless leaflets or prisms, and melts at 80°.

Phenylbenzylbenzenylamidine, $NHPh\cdot CPh\colon N\cdot CH_2Ph$, which is an exception to the law which states that on alkylating an amidine having chemically dissimilar constituents the alkylic group combines with the substituent of higher molecular weight (foregoing abstract), is obtained from benzanilide imidochloride and benzylamine, and melts at 100°; it was first prepared by Beckmann and Fellrath (Abstr., 1893, i, 203), and the methyl derivative is an individual substance having the constitution $NMePh\cdot CPh\colon N\cdot CH_2Ph$, and melting at 67°. It cannot be prepared from benzoylbenzylamine imidochloride and aniline, however, because the latter converts that substance into benzonitrile and benzylaniline, whilst methylaniline resolves it into benzonitrile and benzylmethylaniline.

Benzoylbenzylamine imidochloride, $CPhCl\colon N\cdot CH_2Ph$, is an oil which boils at 104° and 110° under pressures of 60 mm. and 80 mm. respectively. It fumes in the air, and yields benzoylbenzylamine when treated with water. M. O. F.

Amido-Amidines. By CHARLES LAUTH (*Compt. rend.*, 1897, 124, 1105—1106).—*Paranitrobenzorthonitranilide*, crystallises from

toluene in yellow plates, and is sparingly soluble in alcohol and petroleum ; it melts at 216°.

Paramidobenzenylphenyleneamidine, $C_6H_4<\genfrac{}{}{0pt}{}{NH}{-N}>C\cdot C_6H_4\cdot NH_2$, obtained on reducing the foregoing compound with hydrochloric acid and tin, forms long, colourless prisms, readily soluble in alcohol, and sparingly soluble in boiling water; it melts at 240°, and the alcoholic solution exhibits violet dichroism. The *hydrochloride* is sparingly soluble in water, and crystallises in prisms. The base is evidently different from the compound obtained in 1874 by Hubner and Stoever, on nitrating benzenylphenyleneamidine, and reducing the product. Although they describe the substance as melting at 245°, the base obtained by the author on following their instructions melts at 281°; morever, this compound crystallises in spherical aggregates, and the alcoholic solution exhibits green dichroism, whilst the hydrochloride, which dissolves very readily in water, crystallises in plates.

Both bases when diazotised yield products which combine with amines and phenols, producing similar colouring matters; these dye cotton direct in shades which vary from yellow to red or black, according to the nature of the amine or phenol. These colours are indifferent towards chemical agents, but fade when exposed to light.

M. O. F.

Compounds of Hydrogen Chloride with Azophenols. By JOHN T. HEWITT and FRANK G. POPE (*Ber.*, 1897, **30**, 1624—1630).—The authors describe a number of compounds of hydrogen chloride with different azophenols, most of which have been previously obtained by various chemists, although often not in a state of purity. The compounds were obtained by passing a current of dry hydrogen chloride through a benzene solution of different azophenols.

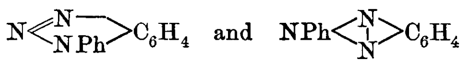
Benzene azophenol hydrochloride, $NPh\!:\!N\cdot C_6H_4\cdot OH,HCl$, crystallises in red needles melting and decomposing at 169°. *Orthochlorobenzeneazophenol hydrochloride* crystallises in dark red prisms melting at about 135°. The corresponding *metachloro*-derivative melts and decomposes at 162—164°; the *para*-compound crystallises in vermilion-red prisms. Orthotolueneazophenol hydrochloride crystallises in minute, dark red needles and prisms softening at 120° and melting at 141°, the para-compound softens at 163°, melts at 169°, and decomposes at 176°. Klein (*Diss. Heidelberg*) gives 172° as the melting point. These hydrochlorides are readily decomposed by water, in most cases yielding the hydrates previously described (Abstr., 1895, i, 353). The hydrochlorides of parachlorobenzeneazophenol and of paratolueneazophenol, however, yield the anhydrous compounds. The authors find that the acetyl, benzoyl, and benzenesulphonyl derivatives of the above azophenols are not capable of combining with hydrogen chloride. The alkylic ethers of the azophenols combine with hydrogen chloride in very much the same way as the azophenols themselves (compare Fischer, *Diss.*). *Benzeneazophenetoil platinochloride*, $(NPh\!:\!NC_6H_4\cdot OEt)_2,H_2PtCl_6$, melts at 186°.

Metachlorobenzeneazophenylic ethylic ether, $C_6H_4Cl\cdot N\!:\!N\cdot C_6H_4\,OEt$, crystallises in flat, yellow needles melting at 51°, and yields a *platino-*

chloride melting and decomposing at 182°. *Parachlorobenzeneazophenylic methylic ether* crystallises in yellow plates melting at 122°. It is readily soluble in all organic solvents with the exception of light petroleum, and yields a *platinochloride* melting and decomposing at 216°. The corresponding *ethylic ether* crystallises in needles melting at 118°; its *platinochloride* melts and decomposes at 201°. J. J. S.

Azimido-, Aznitroso-, Oxazimido-, Oxaznitroso- and Nitrosazimido-compounds. By H. CONRAD C. WILLGERODT (*J. pr. Chem.*, 1897, [ii], **55**, 375—398).—A satisfactory abstract can hardly be made of this paper; it contains an historical account of the subject, and a list of the compounds prepared by the author and his pupils; a change of view regarding the constitution of these compounds is developed, and proposals are made for a new system of nomenclature to be applied to ring compounds containing nitrogen.

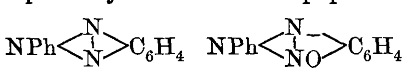
The fact is recalled that the azimides exist in two isomeric forms,



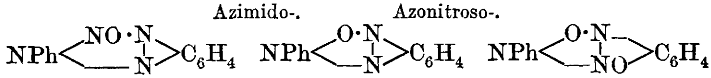
Azimides. Pseudo-azimides.

The azimides are obtained by the action of nitrous acid on orthodiamines; they are basic; and, when they have NH in place of NPh, this hydrogen atom can be replaced by metals, acid radicles, or alkyl groups; the compounds formed in the last case can unite with alkylic iodide, forming quaternary ammonium derivatives. The pseudo-azimides are obtained by oxidising orthamido-azo-compounds, or by the decomposition of the diazo-imides obtainable from these; they have no basic properties.

It is next pointed out that what have hitherto been known as di- and mono-nitrosoazo-compounds ought rather to be regarded respectively as nitro-azimido- and azonitroso-compounds, and that the substances obtainable from them by oxidation ought to be regarded as oxazimido- and oxazonitroso-compounds, the trinitrosoazo-compounds being further regarded as nitrosoazimido-compounds. The following may be taken as types of these five classes of compounds, into which the author divides the substances prepared by himself and his pupils:



Azimido-. Azonitroso-.



Nitrosoazimido-. Oxazimido-. Oxazonitroso-.

These names are read: Phenyleneazimidobenzene, phenyleneazonitrosobenzene, &c. C. F. B.

Combination of Phenylhydrazine with Metallic Chlorides. By JULES VILLE and JOSEPH MOITESSIER (*Compt. rend.*, 1897, **124**, 1242—1244).—When moderately dilute alcoholic solutions of phenylhydrazine are mixed with similar solutions of zinc, nickel, cobalt, cadmium, or magnesium chlorides, compounds are formed of the type

$MCl_2(NHPh\cdot NH_2)_2$. The zinc, nickel, and cobalt compounds crystallise in needles, the cadmium and magnesium compounds in prismatic lamellæ. They are only slightly soluble in cold water, but dissolve somewhat easily in boiling water or alcohol; the solutions give the reactions of phenylhydrazine and the particular metallic chloride. When heated, the compounds decompose before they melt. C. H. B.

Symmetrical Carbamides of the Benzene Series. By PAUL CAZENEUVE and MOREAU (*Compt. rend.*, 1897, **124**, 1102—1104. Compare Abstr., 1896, i, 544).—The general method of preparing symmetrical carbamides of the benzene series, recently described by the authors (*loc. cit.*), has been applied in producing the following compounds.

Di-ψ-cumylcarbamide crystallises from a large quantity of boiling alcohol in colourless needles, insoluble in benzene and water, and only sparingly soluble in ether and chloroform; it volatilises at 280° without undergoing fusion.

Dixylylcarbamide $[Me_2 : NH = 1 : 2 : 4]$ also crystallises in needles, and is insoluble in water and ether, but dissolves in alcohol, chloroform, benzene, and nitrobenzene; the compound melts at 234—235°. 1 : 2 : 3-Xylidine appears to give rise to two substances, a *dixylylcarbamide* melting at 240—241°, which is insoluble in water and ether, and crystallises in the first fraction from alcohol, and a more readily soluble *dixylylcarbamide*, which melts at 207—209°, and occurs in the alcoholic mother liquor. The *dixylylcarbamide* $[Me_2 : NH = 1 : 4 : 2]$ is insoluble in water, cold alcohol, benzene, and ether; it crystallises from a large quantity of boiling alcohol in needles, and volatilises at 285° without melting.

Diparanisylcarbamide crystallises from alcohol in small, white needles and melts at 231—232°. The ortho-compound melts at 182—183°, and not at 174°, as stated by Mulhäuser.

Fatty amines and primary hydrazines also yield carbamides when treated with the carbonic ethers of phenols. M. O. F.

Pentaphenylbiguanide. By J. F. CARL SCHALL (*J. pr. Chem.*, 1897, [ii], **55**, 416).—This substance was described by the author in a communication to the Zurich Chemical Society, before Marckwald described it (Abstr., 1896, i, 30). He will shortly publish a paper on carbodiphenylamide derivatives. C. F. B.

New Synthesis of Aromatic Aldehydes. By LUDWIG GATTERMANN and J. A. KOCH (*Ber.*, 1897, **30**, 1622—1624).—The authors have succeeded in synthesing aromatic aldehydes by passing carbonic oxide and hydrogen chloride into different hydrocarbons in which aluminium chloride and cuprous chloride are suspended. Aldehydes have in this way been obtained from toluene, ortho-, meta-, and para-xylene, ethylbenzene, mesitylene, &c.

A mixture of toluene (30 grams), finely divided, fresh aluminium chloride (45 grams), and cuprous chloride (4 grams) is kept well stirred at a temperature of 20—25°, and through it a mixture of carbonic oxide and hydrogen chloride is kept passing. The carbonic oxide issues from a 10 litre gasholder, and it should take about 3 hours for the whole to pass through the liquid. About 3 litres are absorbed

and the unused portion can be collected and again passed through the mixture. The current of hydrogen chloride should be about half as strong as that of the carbonic oxide. The dark product is poured on to ice, and the aldehyde and any unaltered toluene are driven over with steam; they can then be separated by prolonged shaking with sodium hydrogen sulphite solution. After removing the undissolved toluene by means of a separating funnel, the paratolyl aldehyde can be liberated from the solution by treatment with anhydrous sodium carbonate and purified by distillation with steam. The yield is good.

J. J. S.

Reduction of Aromatic Nitro-derivatives. By ALFRED KIRPAL (*Ber.*, 1897, **30**, 1597—1600).—Bamberger and Friedmann (Abstr., 1895, i, 217) have shown that when metanitrobenzaldehyde is reduced in aqueous solution with zinc dust, a condensation product of the hydroxylamine derivative, and not this derivative itself, is formed. This condensation product, on oxidation, yields metanitrosobenzaldehyde. The author finds that when paranitrobenzaldehyde is reduced in a similar manner neither the hydroxylamine derivate nor a condensation product of this is formed. The product obtained is an extremely unstable substance which is readily oxidised by the atmospheric oxygen to *parazoxybenzaldehyde*. This crystallises from light petroleum or from benzene in yellow needles melting at 194°. Its *phenylhydrazone* crystallises from hot acetone in reddish-yellow needles melting and decomposing at 230°. When oxidised with potassium dichromate and dilute sulphuric acid, the aldehyde yields *parazoxybenzoic acid*. This acid is practically insoluble in all the usual solvents and decomposes at 240°.

J. J. S.

Organic Syntheses depending on Elimination of Halogen Hydride by means of Ferric Chloride. By MARCELLUS NENCKI (*Ber.*, 1897, **30**, 1766—1768).—A description is given of numerous experiments which indicate the value of sublimed ferric chloride as a condensing agent. Its action in general is much milder than that of aluminium chloride, rendering it applicable to syntheses which cannot be effected by this agent.

It is only halogen derivatives which lend themselves to syntheses by means of ferric chloride. Hydroxyketones, for example, are not produced by the action of the substance on acidyl hydrates and phenols, although the use of zinc chloride brings about this result; it is usual to add, in small quantities, one molecular proportion of the condensing agent to the hydrocarbon or phenol, in presence of the acidyl chloride, which will yield the required ketone. In some cases, however, a very small quantity of ferric chloride is sufficient to set up vigorous evolution of hydrogen chloride from a mixture of chloride and hydrocarbon.

When it is required to prepare a hydroxyketone from a polyhydric phenol, it is necessary to employ as many molecular proportions of the acidyl chloride in excess of the theoretical number as will suffice to etherify the hydroxylic groups; for example, in preparing acetophloroglucinol, $COMe\cdot C_6H_2(OH)_3$, four molecular proportions of acetic chloride must be used.

As in the case of aluminium chloride, halogen compounds give

better results with hydrocarbons than with phenols or carboxylic acids, whilst nitrophenol is altogether without action; moreover, acidyl chlorides are more active than alkylic chlorides. In the case of certain phenols, the action of ferric chloride in presence of acidyl chlorides gives rise to diketones; thus resacetophenone, $(COMe)_2C_6H_2(OH)_2$, and gallodiacetophenone, $(COMe)_2C_6H(OH)_3$, are formed from acetic chloride and resorcinol and pyrogallol respectively. M. O. F.

Action of Acidyl Chlorides on Benzene and Monhydric Phenols in Presence of Ferric Chloride. By MARCELLUS NENCKI and E. STOEBER (*Ber.*, 1897, **30**, 1768—1772. Compare foregoing abstract).—When sublimed ferric chloride (7 parts) is added in small quantities to a mixture of benzene (5 parts) and benzoic chloride (7 parts), hydrogen chloride is liberated in considerable volume, and the liquid finally crystallises; the yield of benzophenone amounts to 70 per cent. of the theoretical amount, and an equally satisfactory return of acetophenone is made on using acetic chloride, carbon bisulphide in this case being employed as diluent, and the operation carried out in a reflux apparatus.

Parahydroxyacetophenone is prepared from phenol and acetic chloride; it melts at 108°, and develops a reddish-violet coloration with ferric chloride (compare Klingel, Abstr., 1886, 60). The phenylhydrazone melts at 136°. 1 : 2 : 5- and 1 : 3 : 6-Methylhydroxyacetophenones are produced from acetic chloride with ortho- and meta-cresol respectively, whilst phenol and benzoic chloride fail to yield hydroxybenzophenone, the product consisting of the benzoyl ether of phenol.

Ortho- and para-chlorhydroxyacetophenones are prepared from acetic chloride and ortho- and para-chlorophenols respectively; orthochlorhydroxybenzophenone results from orthochlorophenol and benzoic chloride.

The red colouring matter, $C_{14}H_{10}O_3$, obtained by Bourquin from salicylaldehyde and zinc chloride (Abstr., 1884, 1164) is also produced by the action of ferric chloride. M. O. F.

Halogen-substituted Ketones. By FRANZ KUNCKELL (*Ber.*, 1897, **30**, 1713—1714. Compare this vol., i, 282).—*Orthoxylyl chloromethyl ketone*, $CH_2Cl \cdot CO \cdot C_6H_3Me_2$, crystallises in colourless needles melting at 73—74°, and is readily soluble in alcohol or ether. *Chloromethyl ψ-cumyl ketone* crystallises in colourless plates melting at 76°. By treating toluene with bromacetic bromide according to the method previously given, the author has obtained the same brominated ketone as was previously prepared by the action of bromine on tolyl methyl ketone. *ψ-Cumyl bromomethyl ketone*, $CH_2Br \cdot CO \cdot C_6H_2Me_3$, is obtained when a mixture of ψ-cumene (1·2 part) and bromacetic bromide (3 parts) is added drop by drop to dry carbon bisulphide in which aluminium chloride (3 parts) is suspended. The mixture is kept at the ordinary temperature and then poured into water. The ketone crystallises from its alcoholic solution in colourless prisms melting at 56°.

Pentethylphenyl bromomethyl ketone, $CH_2Br \cdot CO \cdot C_6Et_5$, crystallises in colourless needles and melts at 86°. J. J. S.

Action of Chloracetic Chloride on Phenol and its Ethers. By FRANZ KUNCKELL and FRIEDRICH JOHANNSEN (*Ber.*, 1897, **30**, 1714—1716).—Phenylic chloracetate is obtained when aluminium chloride (50 grams) is gradually added to a mixture of phenol (50 grams), and chloracetic chloride (60 grams) diluted with $1\frac{1}{2}$ times its volume of carbon bisulphide. The mixture is allowed to remain for some time and, is then poured into ice cold water. When double the quantities of acetic chloride and of aluminium chloride given above are used, the chief product is a *parachloromethyl ketone* of *phenylic chloracetate*, $CH_2Cl\cdot CO\cdot C_6H_4\cdot O\cdot CO\cdot CH_2Cl$ [CO : O = 1 : 4]. It crystallises from alcohol in colourless needles, melts at 104°, and is readily soluble in chloroform.

Paranisyl chloromethyl ketone, $OMe\cdot C_6H_4\cdot CO\cdot CH_2Cl$, is obtained in a similar manner by adding aluminium chloride (22·5 grams) to anisoil (15 grams) and chloracetic chloride (22·5 grams) diluted with carbon bisulphide. It crystallises in colourless needles melting at 102°, and when oxidised with potassium permanganate yields anisic acid. When double the above quantities of aluminium chloride and chloracetic chloride are used, *anisyldichlormethyl diketone* (dichloracetylanisoil) $OMe\cdot C_6H_3(CO\cdot CH_2Cl)_2$, melting at 106° is obtained.

Parabromanisyl chloromethyl ketone, $OMe\cdot C_6H_3Br\cdot CO\cdot CH_2Cl$ [OMe : Br = 1 : 4], crystallises in needles melting at 94°.

Phenetyldichloromethyl diketone, $OEt\cdot C_6H_3(CO\cdot CH_2Cl)_2$, crystallises in white plates melting at 108°. Neither of the two diketones are acted on by potassium permanganate. J. J. S.

Action of α-Bromobutyric Chloride on Benzene in the Presence of Aluminium Chloride. By A. COLLET (*Bull. Soc. Chim.*, 1896, [iii], **15**, 1100—1103).—A mixture of α-bromobutyric chloride (50 grams) and dry benzene (200 grams) is gradually added to finely powdered aluminium chloride (75—80 grams) and the action is completed by warming on the water bath. The purified product distils at 154—158° under a pressure of 20 mm. It is a slightly yellow, oily liquid with an irritating odour, and has the composition of phenyl bromopropyl ketone, $CH_2Me\cdot CHBr\cdot CO\cdot C_6H_5$. It reacts with aniline to yield an *anilide*, $CH_2Me\cdot CH(NHPh)\cdot COPh$, melting at 85—86°. The *anilide hydrochloride* is precipitated as a white powder when hydrogen chloride is passed into an ethereal solution of the anilide. The *orthotoluidide* melts at 91°, and the *paratoluidide* at 96°.
J. J. S.

Condensation of Ethylic Salts and Cyanides by Means of Sodium Ethoxide. By REINHOLD WALTHER, and P. G. SCHICKLER, (*J. pr. Chem.*, 1897, [ii], **55**, 305—356).—The reaction was carried out by adding dry sodium ethoxide to the ethylic salt (sometimes in ethereal solution) and finally adding the cyanide; sometimes it was found desirable to keep the mixture cool, at others the reaction was promoted by warming. Occasionally, a mixture of the ethylic salt and the cyanide was added to dry sodium ethoxide; and the whole was sometimes heated in a sealed tube. Water was eventually added to the product, unchanged ethylic salt and cyanide removed by extraction with ether, the residue acidified, and the crude product then

extracted with ether. The normal reaction is the formation of a cyanoketone; for example, $R{\cdot}COOEt + CH_2R'{\cdot}CN = R{\cdot}CO{\cdot}CHR'{\cdot}CN + EtOH$. The cyanoketones are readily hydrolysed by alkalis to the acid $R{\cdot}COOH$ and the original cyanide $R'{\cdot}CH_2{\cdot}CN$; heating with concentrated hydrochloric acid at 150° sometimes converts them into the ketones $R{\cdot}CO{\cdot}CH_2R'$.

Ethylic benzoate could not be made to condense with ethylic cyanide, except that perhaps a small amount of condensation occurred when the two substances were heated for 5 hours at 150° with sodium ethoxide. With benzylic cyanide, however, ethylic benzoate condenses with comparative ease, the yield being 10—20 per cent. of the theoretical. The product, phenyl cyanobenzyl ketone (cyanodeoxybenzoin), $CPhO{\cdot}CHPh{\cdot}CN$, which melts at 87—90°, has an atom of hydrogen replaceable by metals; its *phenylhydrazone* melts at 169°, and its *oxime* at 160—162°; as the latter, when heated at 150° with strong hydrochloric acid, yields no product that will reduce silver nitrate, the substance is probably not a true oxime, but rather *diphenylisoxazolonimide*, $\begin{matrix} CPh \!=\!=\!=\!=\! N \\ | \\ CHPh{\cdot}C(NH) \end{matrix}\!>\!O$. This substance forms, with acetic anhydride, not a mono-, but a *di-acetyl* derivative, melting at 144—145°; in this connection, it may be noticed that phenyl cyanobenzyl ketone itself forms a *monacetyl* derivative melting at 99°. When the cyanoketone is dissolved in alcohol and treated with a drop of ammonia and a little hydrogen peroxide, no amide is obtained, but a substance melting at 95—96°, possibly a physical isomeride of the ketone.

Deoxybenzoincarboxylamide, $CPhO{\cdot}CHPh{\cdot}CONH_2$, can, however, be obtained by dissolving the cyanoketone in sulphuric acid diluted with one-tenth of its volume of water and heating to 120°; it melts at 172—173°. Deoxybenzoincarboxylic acid could not be obtained from the amide in a pure state; its *oxime*, melting at 138—139°, and *phenylhydrazone*, melting gradually between 85° and 150°, can, however, be obtained by treating the amide with hydroxylamine and phenylhydrazine; its *ethylic* salt (hitherto obtained in another way as an oil) melts at 90°. When cyanodeoxybenzoin is treated with diazobenzene chloride, the product is *benzeneazodeoxybenzoin*,

$$CPhO{\cdot}CHPh{\cdot}N_2Ph;$$

it is yellow, and melts at 159°. By passing dry gaseous ammonia for 15 minutes over cyanodeoxybenzoin heated to 160—170° in a U-tube, *imidobenzoylbenzylcyanide* (*phenacetobenzodinitrile*),

$$NH{:}CPh{\cdot}CHPh{\cdot}CN,$$

is formed; this melts at 146°. It is probably formed in small quantity when a mixture of phenylic and benzylic cyanides is treated with sodium, for when the product is dissolved in alcohol and the solution saturated with gaseous hydrogen chloride, some ethylic deoxybenzoincarboxylate (see above) is formed.

Ethylic orthochlorobenzoate hardly condenses, if at all, with benzylic cyanide. The same is true of the metabromobenzoate. Ethylic orthonitrobenzoate yields a small quantity of a product that melts and decomposes at 225—230°, and forms a yellow substance, melting at 80°, when heated with strong hydrochloric acid at 150°; the

reaction is probably not normal. With ethylic metanitrobenzoate, no result was obtained.

With ethylic phthalate, however, benzylic cyanide does yield a product which melts at 164°, and is probably identical with Gabriel's cyanobenzylidenephthalide, $CO<\substack{C_6H_4\\ -O-}>C:CPh\cdot CN$ (Abstr., 1885, 902). With ethylic formate, it also reacts, but the product in this case, *hydroxymethylenebenzylic cyanide* (*phenylcyanohydroxyethylene*),

$$OH\cdot CH:CPh\cdot CN,$$

melting at 157—158°, is probably not a ketone, for it has the reactions of an hydroxy-compound. Strong hydrochloric acid at 150° converts it into phenylacetic acid, ammonia, carbonic oxide, and carbonic anhydride; when oxidised with permanganate in the cold, it yields carbonic anhydride, benzoic acid, and ammonia; with ammonia gas at 160°, it yields yellow *diphenylcyanovinylamine*,

$$NH(CH:CPh\cdot CN)_2,$$

which melts at 175°, and regenerates the original substance when boiled with dilute hydrochloric acid. When treated with methylamine in the same way, it apparently forms some of the analogous *methyl* compound, $NMe(CH:CPh\cdot CN)_2$, melting at 88—89°; but if mixed in alcoholic solution with methylamine hydrochloride, it forms a compound, $NHMe\cdot CH:CPh\cdot CN$, melting at 73—75°, and with aniline in alcoholic solution it forms a yellowish compound, $NHPh\cdot CH:CPh\cdot CN$, melting at 155—156°; the last compound, when treated with nitrous acid, forms a yellow and a red substance,, melting and decomposing at 51° and about 107—110° respectively, but neither of these is the normal nitroso-derivative. Hydroxymethylenebenzylic cyanide further forms a *benzoyl* derivative, melting at 116—117°; with phosphoric chloride, it yields a product which melts at 186—187°, and has possibly the constitution $C_2(CPh\cdot CN)_2$, since it contains no chlorine. With hydroxylamine, it forms a product which melts at 98°, and is apparently an *hydroxyamido*-compound, $OH\cdot NH\cdot CH:CPh\cdot CN$. Its *methylic* salt melts at 90°; its *ethylic* salt was not obtained pure. When heated with diazobenzene chloride, it yields yellow crystals melting at 147—148°.

With ethylic acetate, benzylic cyanide forms *cyanobenzyl methyl ketone* (*acetobenzylic cyanide*), $CMeO\cdot CHPh\cdot CN$; this melts at 89—90°, and with hydroxylamine yields *phenylmethylisoxazolonimide*, melting at 112—113°. With ethylic propionate, *cyanobenzyl ethyl ketone*, $CEtO\cdot CHPh\cdot CN$, melting at 58°, is formed; *phenylethylisoxazolonimide* melts at 70—71°. *Cyanobenzyl propyl ketone*, $CPr^aO\cdot CHPh\cdot CN$, was obtained as an oil; *phenylpropylisoxazolonimide* melts at 107—108°.

Cinnamoylbenzylic cyanide, $CHPh:CH\cdot CO\cdot CHPh\cdot CN + H_2O$, from ethylic cinnamate, benzylic cyanide and sodium ethoxide, is yellow, and melts at 162—163°; by passing hydrogen chloride into its methyl alcoholic solution, *methylic cinnamoylphenylacetate* is obtained.

Methylic cyanide will not condense with ethylic phenylacetate, benzylic cyanide, however, does, forming *phenacetobenzylic cyanide* (*cyanodibenzyl ketone*), $CH_2Ph\cdot CO\cdot CHPh\cdot CN$; this melts at 85—86°. It is reduced by sodium to phenylacetic acid; and with ammonia gas at 170°, it appears to yield dibenzylic cyanide, for the product forms with

hydroxylamine hydrochloride a compound melting at 104—107°. With hydroxylamine hydrochloride in alcoholic solution, it yields *phenylbenzylisoxazolonimide*, which melts at 107—108°, and forms a *hydrochloride* when treated with gaseous hydrogen chloride in ethereal solution. With phenylhydrazine, it yields a compound melting at 119—120°. When dissolved in methylic or ethylic alcohol and treated with gaseous hydrogen chloride, it forms *methylic*, or *ethylic, phenacetophenylacetate*, melting at 66—67° and 77—78° respectively. The *amide* of this acid is obtained by dissolving the cyanide in glacial acetic acid and passing in gaseous hydrogen chloride; it melts at 162—164°, and, when treated with phenylhydrazine acetate in alcoholic or acetic acid solution, forms a compound which melts at about 227°, and is presumably a pyrazolone derivative,

$$CH_2Ph\cdot C{<}\begin{matrix}N\text{——}NPh\\ CHPh\cdot CO\end{matrix}.$$

C. F. B.

Quinone-orthamidobenzoic Acid. By CHARLES ASTRE (*Bull. Soc. Chim.*, 1897, [iii], **15**, 1025—1027. Compare Abstr., 1895, i, 533).—From the purple liquid which deposits quinone-bis-amidobenzoic acid (*loc. cit.*), a more readily soluble product has been separated.

Quinone-orthamidobenzoic acid, $C_6H_3O_2\cdot NH\cdot C_6H_4\cdot COOH$, is obtained by evaporating the alcoholic filtrate from quinone-bis-amidobenzoic acid, and treating the residue with ethylic acetate, which dissolves the substance readily; the compound is black. M. O. F.

Action of Orthamidobenzoic Acid on Trichloroquinone. By CHARLES ASTRE (*Bull. Soc. Chim.*, 1897, [iii], **15**, 1027—1029. Compare Abstr., 1895, i, 533).—*Dichloroquinone-bis-orthamidobenzoic acid*, $C_6Cl_2O_2(NH\cdot C_6H_4\cdot COOH)_2$, is prepared by heating a solution of trichloroquinone in equal parts of alcohol and ethylic acetate with orthamidobenzoic acid dissolved in the same medium for 6 hours at 70—80°; it forms slender needles, and softens at about 300°. The solution in alcohol and ethylic acetate is greenish-yellow. M. O. F.

Action of Orthamidocinnamic Acid on Trichloroquinone. By CHARLES ASTRE and H. STÉVIGNON (*Bull. Soc. Chim.*, 1897, [iii], **15**, 1029—1034. Compare Abstr., 1895, i, 533).—*Dichloroquinone-bis-orthamidocinnamic acid*, $C_6Cl_2O_2(NH\cdot C_6H_4\cdot CH\!:\!CH\cdot COOH)_2$, is obtained by heating trichloroquinone dissolved in equal parts of alcohol and ethylic acetate with orthamidocinnamic acid dissolved in the same medium; the liquid becomes violet, and soon deposits the substance as an amorphous powder, which decomposes before melting. It is insoluble in neutral solvents, and the solution in concentrated sulphuric acid is violet.

Trichloroquinone-orthamidocinnamic acid,

$$C_6Cl_3O_2\cdot NH\cdot C_6H_4\cdot CH\!:\!CH\cdot COOH,$$

is produced along with the foregoing substance, and is obtained by evaporating the filtrate. It is a black powder, and softens at about 55°.

Dichloroquinone-orthimidocinnamic-bis-orthamidocinnamic acid,

$$COOH\cdot CH\!:\!CH\cdot C_6H_4\cdot N\!:\!C_6Cl_2O(NH\cdot C_6H_4\cdot CH\!:\!CH\cdot COOH)_2,$$

is prepared by heating trichloroquinone with orthamidocinnamic acid in glacial acetic acid; the purple liquid is filtered from dichloro

quinone-bis-orthamidocinnamic acid, and evaporated, the residue being washed with boiling water. It is a reddish-brown, amorphous powder.

M. O. F.

Syntheses of Coumarone and of Coumarone Derivatives from Phenoxyacetals. By RICHARD STOERMER (*Ber.*, 1897, 30, 1700—1711.) —In consequence of Hesse's work (this vol., i, 457), the author publishes the following preliminary account of his own researches.

[WITH GIESEKE.]—*β-Naphthoxyacetal*, $C_{10}H_7 \cdot O \cdot CH_2 \cdot CH(OEt)_2$, obtained by heating β-naphthol (9·4 grams), chloracetal (10 grams), and the requisite quantity of sodium ethoxide for 6 hours at 160—170°, is a heavy, colourless oil, boiling at 206—207° (17 mm. pressure), and of sp. gr. = 1·0654 at 14°.

β-Naphthoxyacetaldehyde hydrate, $C_{10}H_7 \cdot O \cdot CH_2 \cdot CH(OH)_2$, obtained by Pomeranz's method, crystallises from its aqueous solution in colourless needles, melts at 87°, and is readily soluble in ether, alcohol, and benzene. It readily reduces both Fehling's solution and also ammoniacal silver nitrate, but is not volatile with steam. Its *semicarbazone* melts at 182°, its *phenylhydrazone* at 145°, and its *oxime* at 123·5°.

β-Naphthoxyacetonitrile, $C_{10}H_7 \cdot O \cdot CH_2 \cdot CN$, was prepared by the action of acetic anhydride on the above oxime according to Lach's method (Abstr., 1884, 1154). When the aldehyde (1 part) is heated to boiling with a solution of zinc chloride (3 parts) in acetic acid (10 parts) for 10 minutes, *β-naphtho-α-furan*, $C_{10}H_6<\substack{O\\CH}>CH$, is obtained. It may be readily purified by distillation in steam, and then forms colourless, glistening needles melting at 60—61°. Hesse (*loc. cit.*) gives the melting point as 65°. It yields a *picrate* crystallising in reddish-yellow needles and melting at 141°. *β-Naphthofurancarboxylic acid*, $C_{10}H_6<\substack{O\\CH}>C \cdot COOH$, forms colourless crystals melting at 191—192°, and is readily soluble in ether, alcohol, and benzene.

α-Naphthoxyacetal is also an oil, boiling at 207—208° (18 mm. pressure), of sp. gr. = 1·0698 at 14° and n_D = 1·561 at 16°. The corresponding *aldehyde* melts at 86° and yields a *semicarbazone* (m. p. 149—150°), a *phenylhydrazone*, and an *oxime* (m. p. 108°). α-Naphthofuran, contrary to Hesse's statement, could only be obtained as an oil of sp. gr. = 1·1504 at 14°; it yields a *picrate* melting at 113°.

Coumarone itself has been synthesised by heating phenoxyacetaldehyde with a solution of zinc chloride in glacial acetic acid.

[WITH H. SCHMIDT.]—The following compounds, which have also been obtained by Hesse, have been prepared, but in most cases the melting and boiling points do not agree with those given by Hesse. Paratolyloxyacetal boils at 270° at the ordinary pressure, but at the same time undergoes slight decomposition; at 20° mm. pressure, its boiling point is 157—158° and its sp. gr. = 0·9959 at 22°. Hesse gives the boiling point at 262—263°. Paratolyloxyacetaldehyde hydrate melts at 58° (Hesse 65°), and the *aldehyde* itself, $C_6H_4Me \cdot O \cdot CH_2 \cdot COH$, obtained by heating the hydrate under reduced pressure, distils at 126° under 27 mm. pressure. The semicarbazone melts at 177°, the phenylhydrazone at 111° (Hesse 106°), and the oxime at 99° (Hesse 68°). The oxime, when boiled with

acetic anhydride, yields *paratolyloxyacetonitrile*, $C_6H_4Me{\cdot}O{\cdot}CH_2{\cdot}CN$, which crystallises in large, broad needles melting at 40°. Metatolyloxyacetal is an oil boiling at 267—268° (Hesse 262—263°), and its sp. gr. = 0·9728 at 14°. Metatolyloxyacetaldehyde hydrate melts at 57° (Hesse 56°), and its oxime at 87° (Hesse 82°). *Metatolyloxyacetonitrile* is a yellow liquid boiling at 254°. *Orthotolyloxyacetal* boils at 262°, and its sp. gr. = 0·9928 at 22°; the *aldehyde hydrate* forms colourless needles melting at 74°, and has the same objectionable odour as its isomerides; the *semicarbazone* melts at 151°, and the *oxime* at 117°.

By heating each of the three tolyloxyacetals (1 part) separately with a solution of zinc chloride (3 parts) in glacial acetic acid (10 parts), the authors have succeeded in synthesising the three methylcoumarones. *Paramethylcoumarone*, $C_6H_3\overset{(4)}{Me}<\genfrac{}{}{0pt}{}{\overset{(1)}{-O-}}{CH}>CH$, is a colourless oil, boiling at 197—199°, of sp. gr. = 1·0467 at 15°, and refractive index = 1·547 at 16°. With sulphuric acid, it yields a dark, brown-red coloration, and its *picrate* crystallises in yellow needles melting at 73°. *Metamethylcoumarone* is also an oil boiling at 195—196°; its sp. gr. = 1·056 at 16°, and its refractive index = 1·554 at 16°. With sulphuric acid, it yields a brilliant, dark purple coloration, and its *picrate* melts at 72°. *Orthomethylcoumarone* boils at 190—191°, and yields a *picrate* melting at 109°.

[With SCHROEDER.]—*Unsymmetrical ortho-xylenoxyacetal*,

$$C_6H_3Me_2{\cdot}O{\cdot}CH_2{\cdot}CH(OEt)_2\ [Me_2 : O = 1 : 2 : 4],$$

boils under 20 mm. pressure at 168°, and its sp. gr. = 0·992 at 16°. The corresponding *aldehyde hydrate*, $C_6H_3Me_2{\cdot}O{\cdot}CH_2{\cdot}CH(OH)_2$, has an extremely strong odour, melts at 38°, and is readily soluble in water, alcohol, or ether. The *oxime* melts at 99°, the *phenylhydrazone* at 68°, and the *semicarbazone* at 187°. *Unsymmetrical metaxylenoxyacetal* $[Me_2 : O = 1 : 3 : 4]$ boils at 273°, and its sp. gr. = 0·995 at 16°. The *aldehyde hydrate* has a strong odour of lemons, and melts at 62°. The *oxime* melts at 98°, the *phenylhydrazone* at 91—92°, and the *semicarbazone* at 116—117°. *Paraxylenoxyacetal* $[Me_2 : O = 1 : 4 : 2]$ boils at 278—279°, and its sp. gr. = 0·972 at 16°; the *aldehyde hydrate* melts at 63—64°, the *oxime* at 114°, and the *semicarbazone* at 104°.

Parethylphenoxyacetal, $C_6H_4Et{\cdot}O{\cdot}CH_2{\cdot}CH(OEt)_2$ $[Et : O = 1 : 4]$, distils at 288—289°, and when boiled with very dilute sulphuric acid yields *parethylphenoxyacetaldehyde hydrate* melting at 49°, the *oxime* of which melts at 104°.

Metaparadimethylcoumarone, obtained from the unsymmetrical orthoxylenoxyacetal, boils at 221°, its sp. gr. = 1·06 at 15°, and with concentrated sulphuric acid it gives a claret coloration. Its *picrate* melts at 65—66°. *Orthoparadimethylcoumarone* is an oil with a penetrating odour, and boils at 221—222°. At 16°, its sp. gr. = 1·036, and its refractive index 1·5412; with concentrated sulphuric acid, it gives a methyl-violet coloration. Its *picrate* melts at 78—79°. *Orthometadimethylcoumarone* boils at 216°, its sp. gr. = 1·041 at 16°, and its refractive index = 1·549 at the same temperature. Its *picrate* melts at 101°. *Parethylcoumarone* boils at 217—218°, and with sulphuric acid gives a bluish-pink coloration.

ψ-Cumenoxyacetal, $C_6H_2Me_3 \cdot O \cdot CH_2 \cdot CH(OEt)_2$, boils at 290°, and its sp. gr. = 0·9886. The corresponding *aldehyde hydrate* melts at 81°, and yields an *oxime* melting at 110°.

1 : 3 : 4-*Trimethylcoumarone* is a colourless oil boiling at 236°; it solidifies when cooled, but melts again below 18°. Its sp. gr. = 1·0205 at 21°, and its refractive index at the same temperature = 1·547. It yields a *picrate* melting at 105°. J. J. S.

Further Syntheses of Coumarone Derivatives. By RICHARD STOERMER (*Ber.*, 1897, **30**, 1711—1712. Compare previous abstract.) —*a-Acetylcoumarone*, $C_6H_4{<}{}^{O}_{CH}{>}CAc$, is obtained by the action of chloracetone on the dry sodium salt of acetaldehyde suspended in benzene. The benzene is distilled off, and then the acetylcoumarone can be purified by steam distillation. It crystallises from its benzene solution in thick plates melting at 74—75°, is readily soluble in most organic solvents, and moderately in water. When fused with potash, it yields coumarone, and when oxidised with potassium permanganate, it yields coumarilic acid; it also reacts with hydroxylamine and phenylhydrazine. Ethylic γ-bromacetate and chloracetaldehyde also appear to react with the sodium derivative of salicylaldehyde. Phenoxyacetic acid, $C_6H_5 \cdot O \cdot CH_2 \cdot COOH$, when treated with a solution of zinc chloride in acetic acid, reacts in very much the same way as the corresponding aldehyde (see previous abstract), and yields keto-coumaran, $C_6H_4{<}{}^{O}_{CO}{>}CH_2$. J. J. S.

Phenylglyceric Acids. By JOSEF PLÖCHL and BERTRAM MAYER (*Ber.*, 1897, **30**, 1600—1614).—Anschütz and Kinicutt (Abstr., 1878, 981; 1879, 644), by treating ethylic dibromohydrocinnamate with silver benzoate and then hydrolysing with alcoholic potash, obtained a phenylglyceric acid melting at 117°. Lipp (Abstr., 1883, 994) obtained a phenylglyceric acid melting at 143—144°, but regarded his acid as identical with Anschütz's since it gave the same dibenzoate when heated with benzoic chloride. Fittig and Ruer obtained the same acid melting at 141—142° by oxidising cinnamic acid in the cold with potassium permanganate (Abstr., 1892, 986). The authors have repeated Anschütz and Kinnicutt's experiments, and find that the acid previously described as melting at 117° really melts at 120—121°. It yields a *phenylhydrazide* melting at 177°, and when treated with fuming hydrobromic acid yields *phenyl-β-bromolactic acid*, $CHPhBr \cdot CH(OH) \cdot COOH$, melting and decomposing at 156—157°. The latter acid is readily soluble in alcohol, ether, or warm chloroform, and only sparingly in benzene or warm water; in the latter case, decomposition readily ensues with the formation of phenylacetaldehyde. When heated at about 40° with acetic anhydride, phenylglyceric acid (m. p. 120—121°) yields a *monacetyl* derivative melting at 158°. The following salts have been prepared in a crystalline form: *Calcium* salt, $(C_9H_9O_4)_2Ca + 3H_2O$; *zinc* salt, with $4H_2O$; *copper* salt, with $2H_2O$, and the *lead* salt. The authors also confirm Fittig and Ruer's work on the phenylglyceric acid melting at 141—142° and find that this acid is quite distinct from the one melting at 120—121°. It yields a *phenylhydrazide* which crystallises

from dilute alcohol in yellow prisms melting at 215°. With fuming hydrobromic acid, it yields a phenylbromolactic acid melting at 164—165°, and agreeing with the lactic acid obtained from the isomeric phenylglyceric acid in all its properties with the exception of melting point. The *monacetate* of the acid melting at 141—142° crystallises in glistening scales and melts at 93·5°. *Ethylic phenylglycerate dibenzoate,* obtained from the ethylic salt of the acid melting at 141—142° by the Schotten-Baumann method, crystallises in silky needles melting at 85°. The corresponding derivative of the acid melting at 120—121° melts at 109° (Anschütz and Kinnicutt). The *zinc* salt of the acid melting at 141—142° crystallises with $4H_2O$, the *cadmium* salt also with $4H_2O$ and the *copper* salt with H_2O. The authors find that Lipp's method (*loc. cit.*) gives a good yield of the acid melting at 120—121° and but a small amount of the isomeric acid melting at 141—142°. The fact that Lipp does not mention the acid melting at 120—121° is explained by the fact that it is readily soluble in ether, whereas the isomeric acid is not.

The acid of lower melting point can readily be decomposed into its optically active constituents, either by means of its *strychnine* salt (m. p. 144°), or by the action of *Penicillium glaucum* which destroys the dextro- acid more readily than the lævo-. The two *optically active phenylglyceric* acids crystallise in plates melting at 166—167°. They are much less soluble in water than the racemic acid, and their rotatory powers are respectively $[\alpha]_D = +31·08°$ and $[\alpha]_D = -30·23°$. The *zinc, calcium,* and *copper* salts of the two active acids are described; they crystallise much more readily than the salts of the racemic acid. All attempts to decompose the acid melting at 141—142° into optically active constituents have so far failed.

When the ethylic salt of the acid of higher melting point is benzoylated at 150° and the resulting dibenzoate hydrolysed with alcoholic potash, the acid melting at 120—121° is formed. If, on the other hand, the dibenzoate of the ethylic salt obtained from the acid melting at 120—121° is hydrolysed with strong aqueous sodium hydroxide, the acid melting at 141—142° is formed together with a small quantity of the isomeric acid. The authors conclude with a comparison of these acids with the tartaric acids and hydrobenzoins. J. J. S.

Caffetannic Acid. By PAUL CAZENEUVE and E. HADDON (*Compt. rend.*, 1897, **124**, 1458—1460).—Since the investigations of Hlasiwetz, caffetannic acid has been usually regarded as having the formula $C_{15}H_{18}O_8$, but the authors, from a study of the behaviour of the substance towards phenylhydrazine, conclude that it has the composition $C_{21}H_{28}O_{14}$, and ascribe to it the constitutional formula $COOH·CH:CH·C_6H_3(O·C_6H_{11}O_5)_2$.

The *osazone* of caffetannic acid, $C_{45}H_{48}N_8O_{10}$, crystallises in yellow needles very sparingly soluble in alcohol, and melts at 180°; it is insoluble in most media, and is so sparingly soluble in phenol and naphthalene that no determinations of molecular weight have been possible.

The sugar, $C_6H_{12}O_6$, obtained on hydrolysing caffetannic acid, will be described in a subsequent paper. M. O. F.

Caffetannic Acid (Glucosylcaffeic Acid) and its Decomposition into Caffeic Acid, Vinylcatechol, and Catechol. By HERMANN KUNZ-KRAUSE (*Ber.*, 1897, 30, 1617—1622).—Both caffetannic acid and matétannic acid, when hydrolysed, yield a syrupy sugar and caffeic acid (dihydroxycinnamic acid). This acid, when heated at 200°, readily loses carbonic anhydride, yielding vinylcatechol (3 : 4-dihydroxycinnamene), the decomposition at this temperature being quantitative. A characteristic reaction for vinylcatechol is the one previously mentioned (*Arch. Pharm.*, 1893, 231, 635). This reaction is also given by Tiemann and Will's hesperetol or vinylcatechol paramonomethyl ether (Abstr., 1881, 739). The carmine-red coloration with sulphuric acid therefore appears to be characteristic of 3 : 4-dihydroxycinnamene and its ethers. The author has only succeeded in obtaining the vinylcatechol as an amorphous powder; it is a somewhat unstable substance, for when distilled under a pressure of 12 mm. it is decomposed, the chief product being catechol. The author thinks it probable that caffetannic acid is distributed throughout the vegetable kingdom in very much the same manner as choline. J. J. S.

Synthesis of Aromatic Acids and Aldehydes by means of Aluminium Chloride. By LOUIS BOUVEAULT (*Bull. Soc. Chim.*, 1897, [iii], 15, 1014—1021).—The following method of preparing phenylglyoxylic acid is one of general application in the aromatic series. Crystallised benzene (90 grams) is heated with dry carbon bisulphide (200 grams) and aluminium chloride (140 grams) in a reflux apparatus at 40—50°, and treated with the chloride of monethylic oxalate (136 grams), which is added drop by drop; a crystalline double compound is formed, and on treating this substance with water, ethylic phenylglyoxylate (120—130 grams) is set free. Hydrocarbons, and the alkyl ethers of monhydric and polyhydric phenols may be employed in this method of synthesis, which is not applicable, however, to free phenols or their acidyl derivatives. When phenol ethers are used, it is advantageous to add the aluminium chloride in small quantities at a time to the carbon bisulphide solution containing the chloride of monethylic oxalate. The ethylic phenylglyoxylate (or its homologue) obtained by this process is hydrolysed with a hot 10 per cent. aqueous solution of caustic soda, as the alcoholic agent induces secondary changes.

There is no difficulty in converting phenylglyoxylic and its homologues, R·CO·COOH, into the respective acids, R·COOH, although transformation into the aldehydes, R·COH, is less easy to accomplish. When these compounds are heated alone, carbonic anhydride and oxide are generated, along with a mixture of the acid and aldehyde corresponding to the substance employed; but owing to the almost exclusive production of the acid in most cases, this is not the most satisfactory method of procedure. If the acid is required, it is better to treat the compound with aqueous hydroxylamine hydrochloride, which gives rise to the oxime R·C(NOH)·COOH; elimination of carbonic anhydride and water from this compound under the influence of heat converts it into the nitrile R·CN, which can be hydrolysed to the acid.

In order to prepare the aldehyde, phenylglyoxylic acid or the homologue is heated with aniline, which forms the compound

R·C(NPh)·COOH, and this, at the temperature of the boiling base, passes into the phenylimide R·CH:NPh; dissolution of this compound in hot 25 per cent. sulphuric acid eliminates aniline, and sets free the aldehyde.

Attempts have been made to substitute hydrazine and paramidophenol for aniline in the foregoing process. Although these compounds undergo condensation with phenylglyoxylic acid and its derivatives, yielding substances from which carbonic anhydride is eliminated by heat, the yield of aldehyde obtained from the product is very poor.

M. O. F.

Acetylsalicylic Acid. By M. Białobrzeski and Marcellus Nencki (*Ber.*, 1897, **30**, 1776—1779).—*Acetylsalicylic acid*,

$$COMe{\cdot}C_6H_3(OH){\cdot}COOH,$$

is obtained by adding small quantities of ferric chloride (100 grams) to a mixture of salicylic acid (80 grams) and acetic chloride (100 grams). It is sparingly soluble in water, and dissolves readily in alcohol, ether, benzene, and chloroform; it melts at 210°, and develops a red coloration with ferric chloride. The *oxime* crystallises in needles, and melts at 175°; ferric chloride develops a violet coloration. The *phenylhydrazone* forms yellow needles, and melts and decomposes at 212°; a violet coloration is produced by ferric chloride with this derivative also. The *sodium* salt crystallises in white plates containing $3H_2O$, and the *potassium* salt forms yellowish, microscopic needles containing $\frac{1}{2}H_2O$; the *ammonium* and *barium* salts contain $1H_2O$ and $2H_2O$ respectively.

The antiseptic action of salicylic acid is considerably impaired by the introduction of the acetyl group into the benzene ring. The growth of yeast cells, typhus bacilli, and erysipelas cocci is unchecked by the substance, and the animal organism suffers no inconvenience from its assimilation.

M. O. F.

Diphenacylcyanacetic Acid. By C. Timothée Klobb (*Bull. Soc. Chim.*, 1897, [iii], **15**, 1008—1014. Compare Abstr., 1896, i, 126).—Whilst cold aqueous potash is without action on ethylic diphenacylcyanacetate, the boiling solution gives rise to a secondary action, producing ammonia and diphenacylacetic acid; alcoholic potash, on the other hand, yields a very different product (see below), and the method of hydrolysing ethereal salts of other cyano-acids (*loc. cit.*) must be adopted in the present case.

Diphenacylcyanacetic acid, $(COPh{\cdot}CH_2)_2C(CN){\cdot}COOH$, is obtained by treating an acetone solution of the ethylic salt with the calculated amount of caustic potash dissolved in alcohol; hydrolysis takes place immediately at the ordinary temperature, and the liquid, without delay, is largely diluted, and acidified with sulphuric acid. The acid has a bitter taste, and crystallises in small, colourless prisms melting at 172—174°. Alcoholic potash forms a deep blue solution, aqueous alkalis yielding a pale red solution, which rapidly becomes turbid and deposits a red, flocculent precipitate; cold concentrated sulphuric acid dissolves it without developing colour, but on carefully heating the solution it becomes red, and finally emerald green, whilst a cinnabar-red compound, insoluble in water, but forming a blue solution in alcoholic potash, is

precipitated on pouring it into water. The alkali salts slowly become pale red on exposure to light. The *sodium* salt contains $2H_2O$, and forms white, nacreous leaflets; it is difficult to obtain the substance colourless, and its solutions become red when heated. The *ammonium* salt contains $2\frac{1}{2}H_2O$, and the *barium* salt, which is insoluble in water and alcohol, contains $1H_2O$ after being dried in a vacuum.

The *compound*, $C_{18}H_{15}NO_3$, is obtained by adding caustic soda to a boiling solution of ethylic diphenacylcyanacetate, and cooling the liquid by repeated decantation, continuing this process until the blue coloration no longer deepens; the solution is then largely diluted, and acidified with sulphuric acid. The bright red precipitate acquires a darker shade when dried in the desiccator. It is insoluble in water, but dissolves freely in alcohol, ether, chloroform, and benzene, forming solutions which redden blue litmus; bright sunlight decolorises it completely. It becomes brown at 140°, and melts and blackens at about 170°. The solution in concentrated sulphuric acid is emerald green, alcoholic potash developing a blue coloration. The production of this substance from ethylic diphenacylcyanacetate seems to depend on the influence of atmospheric oxygen. M. O. F.

An Additive Compound of Aniline with Ethylic Dicarboxyglutaconate. By MAX GUTHZEIT (*Ber.*, 1897, **30**, 1757—1759).—Ruhemann and Morrell (Abstr., 1895, i, 20), and simultaneously Band (Abstr., 1895, i, 561), have shown that aniline resolves ethylic dicarboxyglutaconate into ethylic malonate and ethylic anilidoethylenedicarboxylate; by suitably modifying the conditions of the experiment, the author has isolated the intermediate product of the action.

Ethylic β-anilidodicarboxyglutarate,

$$(COOEt)_2CH\cdot CH(NHPh)\cdot CH(COOEt)_2,$$

is obtained by gradually adding ice-cold aniline (3—5 mols.) to a well cooled 14 per cent. solution of the ethereal salt in ether, and agitating the liquid during the operation; after 24 hours, the solution is extracted with dilute hydrochloric acid, and the ethereal liquid, on evaporation, deposits an oil which rapidly solidifies. It crystallises from light petroleum in clusters of small prisms, and melts at 46—47°; it is feebly basic, and forms a brownish-red, semi-solid *hydrochloride*, which evolves hydrogen chloride in the desiccator. Although ethylic anilidoethylenedicarboxylate melts at 48°, it differs from the additive compound in crystalline form and in its colour reactions; whilst the former substance dissolved in concentrated sulphuric acid develops a blue coloration with ferric chloride and potassium dichromate, changing to deep red in the latter case, a solution of the additive compound becomes yellow with ferric chloride, and dirty brown with potassium dichromate.

The substance dissolves in cold aniline, and after 14 days the solution contains ethylic malonate and ethylic anilidoethylenedicarboxylate; the same result is in part effected when the ethereal salt is distilled in a current of steam (compare Goldstein, Abstr., 1895, i, 470). M. O. F.

Benzenesulphonamides. By CH. RABAUT (*Bull. Soc. Chim.*, 1897, [iii], **15**, 1035—1037. Compare Abstr., 1895, i, 595).—*Benzene-*

sulphoparatoluidide, $C_6H_5\cdot SO_2\cdot NH\cdot C_6H_4Me$, obtained by the action of benzenesulphonic chloride on paratoluidine, forms white crystals melting at 122° (compare *Ber.*, 1876, **9**, 427). The dinitro-derivative is produced by the action of boiling nitric acid of sp. gr. 1·10, and melts at 178—179°; when heated with concentrated hydrochloric acid in sealed tubes, it yields dinitroparatoluidine (m. p. 166°), so that it is identical with the compound described by Lellman (Abstr., 1883, 800).

Benzenesulphometaxylidine, $C_6H_5\cdot SO_2\cdot NH\cdot C_6H_3Me_2$, dissolves very readily in alcohol, and forms white crystals melting at 128—129°. The *nitro*-derivative [$Me_2 : NH : NO_2 = 1 : 3 : 4 : 5$] is a yellow compound which crystallises from alcohol and melts at 152—153°; concentrated hydrochloric acid converts it into nitrometaxylidine (m. p. 68—69°). The *amido*-derivative forms white needles, and melts at 140—141°.

Benzenesulphoparaxylidine forms white crystals melting at 138—139°. The *dinitro*-derivative is obtained by the prolonged action of boiling nitric acid of sp. gr. 1·10, and melts at 174—175°. The *diamido*-derivative separates in white crystals which become brown in air; it melts at 180—181°.

These sulphonamides are readily oxidised by potassium permanganate. M. O. F.

The Second Stilbene. By ROBERT OTTO and FRITZ STOFFEL (*Ber.*, 1897, **30**, 1799—1800. Compare Abstr., 1896, i, 242).—It has been shown (*loc. cit.*) that α-stilbene dibromide (m. p. 237°) yields stilbene when treated with sodium phenylmercaptide. Wislicenus and Seeler (Abstr., 1896, i, 98) have pointed out that whilst α-stilbene dibromide may be considered to be derived from plane-symmetrical stilbene $\begin{matrix}Ph\cdot C\cdot H\\ \| \\ Ph\cdot C\cdot H\end{matrix}$, and therefore expressed by the meso-tartaric formula $\begin{matrix}Ph\cdot CBrH\\ | \\ H\cdot CPhBr\end{matrix}$, the β- (*iso*) compound (m. p. 110°) probably has the racemic configuration $\begin{matrix}Ph\cdot CBrH\\ | \\ Br\cdot CHPh\end{matrix}$, being derived from the central symmetrical hydrocarbon $\begin{matrix}Ph\cdot C\cdot H\\ \| \\ H\cdot C\cdot Ph\end{matrix}$. Studying the behaviour of the *iso*-dibromide (m. p. 110°) towards sodium phenylmercaptide, the authors have obtained an oil which they believe to consist of the second stilbene; this product yields the α-dibromide when treated with the halogen in ether. M. O. F.

Phenyl Derivatives of Ethane and Ethylene. By HEINRICH BILTZ (*Annalen*, 1897, **296**, 219—260. Compare Abstr., 1893, i, 718). —The author has shown (*loc. cit.*) that the action of aluminium chloride on benzene and chloral in carbon bisulphide gives rise to tetraphenylethane, tetraphenylethylene, triphenylvinylic alcohol, and diphenyldichlorethylene. The present paper describes the further investigation of these substances and their derivatives.

Tetraphenylethane, $CHPh_2\cdot CHPh_2$, crystallises from glacial acetic acid in long, colourless, prismatic needles, and melts at 207·5° (uncorr.), or at 211° when a short thermometer is used; it boils at 358—362°

(uncorr.), or at 379—383° (corr.). The hydrocarbon resembles in every particular the product obtained by Anschütz from stilbene dibromide.

Tetraparanitrotetraphenylethane, $C_2H_2(C_6H_4\cdot NO_2)_4$, is prepared by dissolving the finely powdered hydrocarbon in 20 parts of fuming nitric acid at 30—40°; the product is insoluble in alcohol, but crystallises from aniline in orange rhombohedra containing 4 mols. of the base. If the concentrated solution in aniline is cooled rapidly, colourless, monoclinic needles separate, consisting solely of the nitro-compound, which passes into the rhombohedral form when kept for some days in the mother liquor; the substance crystallises from nitrobenzene in prisms, and melts and decomposes at 300° (uncorr.), or at 337·5—338·5° (corr.). Tetranitrotetraphenylethane is indifferent towards concentrated sulphuric acid or an acetic acid solution of chromic acid, even resisting the action of fuming nitric acid at 110°; when chromic acid is added to a solution of the substance in concentrated sulphuric acid at 50°, however, paradinitrobenzophenone is produced.

Tetraparamidotetraphenylethane, $C_2H_2(C_6H_4\cdot NH_2)_4$, obtained by reducing the nitro-derivative with tin and hydrochloric acid, crystallises in brown, monoclinic prisms; it melts at 264° (uncorr.), or at 272° when a short thermometer is employed. The *stannichloride* crystallises from water in small, lustrous needles, and the *acetyl* derivative separates from dilute acetic acid in colourless crystals melting at 336—337° (corr.); the base is readily diazotised, and the product yields colouring matters with phenols and amines.

Tetraphenylethylene crystallises from benzene after addition of alcohol in thin, highly refractive plates, and melts at 221° (uncorr.), or at 223·5—224·5° when a short thermometer is used; it does not form an additive compound with bromine, but yields a substitution product instead.

Tetraparabromotetraphenylethylene, $C_2(C_6H_4Br)_4$, is obtained on adding bromine to a solution of tetraphenylethylene in carbon tetrachloride, hydrogen bromide being evolved; it crystallises in long needles from carbon tetrachloride containing a small quantity of alcohol. The substance dissolves very readily in benzene, but more sparingly in carbon tetrachloride or glacial acetic acid, and is insoluble in alcohol; it melts at 248—249° (uncorr.), or at 253—255° on a short thermometer. Oxidation with chromic acid dissolved in glacial acetic acid converts the bromo-derivative into dibromobenzophenone (m. p. 175°).

Tetranitrotetraphenylethylene, $C_2(C_6H_4\cdot NO_2)_4$, is obtained by dissolving the hydrocarbon in concentrated nitric acid below 5°; it dissolves very readily in benzene and in nitrobenzene, and has not been crystallised, the amorphous compound melting at about 100°. Oxidation of the nitro-derivative gives rise to two products, according to the conditions under which the operation is conducted.

Tetranitrotetraphenylethylene oxide (*Tetranitro-α-benzopinacolin*), $O<\begin{matrix}C(C_6H_4\cdot NO_2)_2\\ |\\ C(C_6H_4\cdot NO_2)_2\end{matrix}$, is prepared by adding chromic acid to a solution of

the nitro-derivative in glacial acetic acid at 90°, and maintaining the temperature of the liquid at 80° during 4 hours; it dissolves sparingly in boiling glacial acetic acid, and crystallises from this solvent in colourless, triclinic needles. It melts at 294° (uncorr.), and at 298—299° on a short thermometer. It is not identical with *tetranitro-β-benzopinacolin*, $C_{26}H_{16}N_4O_9$, obtained on nitrating α- and β-benzopinacolins; the amorphous substance sinters at 120—140°, and has not been crystallised. Alcoholic potash develops a deep violet coloration, which ultimately becomes brownish.

Tetranitrotetraphenylethylene dioxide, $\begin{matrix} O\cdot C(C_6H_4\cdot NO_2)_2 \\ | \quad | \\ O\cdot C(C_6H_4\cdot NO_2)_2 \end{matrix}$, is obtained from the mother liquor of the oxide, and may be prepared by oxidising tetranitrotetraphenylethylene with chromic acid in glacial acetic acid at 115—130°; it crystallises from glacial acetic acid in pale yellow, lustrous scales, and melts and decomposes at 183° (uncorr.). It is decomposed by concentrated sulphuric acid, which forms a deep yellow solution. The dioxide is somewhat soluble in fused naphthalene, but does not dissolve in boiling benzene.

Diphenyldichlorethylene, $CPh_2\!:\!CCl_2$, crystallises from benzene in flattened plates, consisting of aggregates of lamellæ; it melts at 80°, and boils at 315° (uncorr.), or at 336° (corr.). The solution in warm concentrated sulphuric acid is yellow, becoming dark green on further heating, this colour changing to violet black and brownish-red as the temperature approaches the boiling point of the acid. The substance gives rise to additive compounds with bromine and chlorine.

Triphenylvinylic alcohol, $CPh_2\!:\!CPh\cdot OH$, crystallises from alcohol in lustrous, monoclinic plates, and melts at 136° (uncorr.); oxidation with an alkaline solution of potassium permanganate gives rise to benzophenone and benzoic acid, the same products being obtained with an acetic acid solution of chromic acid. Hydrolysis with alcoholic potash resolves the alcohol into diphenylmethane and benzoic acid. The *acetyl* derivative crystallises from dilute acetic acid in monoclinic prisms, and melts at 104·5—105·5°; attempts to prepare a benzoyl derivative by the Baumann-Schotten method and by Deninger's modification were, however, fruitless.

Tribromophenyltribromethane, $C_2Br_3(C_6H_4Br)_3$, obtained by the direct action of bromine on the alcohol, crystallises from benzene in slender needles melting at 245° (corr.). A simple additive compound of triphenylvinylic alcohol with bromine has not been obtained.

Triphenylethane, $CHPh_2\cdot CH_2Ph$, is prepared by reducing triphenylvinylic alcohol with hydriodic acid and phosphorus at 180°; it crystallises in colourless leaflets, and melts at 53·5—54·5°. A compound obtained from benzene, chlorodiphenylethane, and aluminium chloride has been described by Waas (Abstr., 1882, 1209) as having this constitution; it is, however, an oil which boils above 360°.

Phenylbenzoin ethyl ether, $COPh\cdot CPh_2\cdot OEt$, is obtained by heating triphenylvinylic alcohol with an alcoholic solution of hydroxylamine hydrochloride in a reflux apparatus, ammonium chloride being also produced; it crystallises in colourless, rhombic prisms. Alcoholic soda resolves the substance into benzhydrol ethyl ether, $CHPh_2\cdot OEt$, and benzoic acid.

The portion of the crude product from chloral and benzene which boils at 400°, crystallises immediately in the receiver; it melts at 233° (uncorr.), and appears to be identical with the hydrocarbon, $C_{26}H_{18}$ (possibly phenylbenzyldiphenylenemethane), obtained by Hanriot and St. Pierre by reducing a substance prepared from benzoic chloride and the potassium derivative of triphenylmethane (Abstr., 1889, 882). Oxidation with chromic acid in glacial acetic acid converts it into the compound, $\begin{matrix}C_6H_4\\ | \\ C_6H_4\end{matrix}\!\!>CPh\cdot COPh$ (m. p. 172°), obtained by Hanriot and St. Pierre in the manner described.

The mother liquors accumulated during the investigation of the products from chloral, benzene, and aluminium chloride, were found to contain phenyldichlorethylene, diphenylmethane, triphenylmethane, and a very small quantity of benzoic acid. M. O. F.

Sulphoketones of the Naphthalene Series. By JULIUS TROEGER and F. BOLM (*J. pr. Chem.*, 1897, [ii], **55**, 398—416).—By heating chloracetone, $CH_3\cdot CO\cdot CH_2Cl$, with a naphthalenesulphinate, $C_{10}H_7\cdot SO_2M$, in aqueous alcoholic solution, a naphthylsulphonacetone,

$$CH_3\cdot CO\cdot CH_2\cdot SO_2\cdot C_{10}H_7,$$

is obtained; this can be brominated in acetic acid solution, and then yields a naphthylsulphobromacetone, $CH_2Br\cdot CO\cdot CH_2\cdot SO_2\cdot C_{10}H_7$, which will react with a sulphinate, $R\cdot SO_2M$, yielding a disulphone,

$$R\cdot SO_2\cdot CH_2\cdot CO\cdot CH_2\cdot SO_2\cdot C_{10}H_7.$$

Compounds of this last type exhibit the distinctive ketonic reactions in a much less degree than usual; often they only react with hydroxylamine or phenylhydrazine when heated with these substances under pressure. β-Naphthyl derivatives are much more easily prepared than the isomeric α-compounds, as the latter crystallise with difficulty; of the disulphones, the naphthyl-tolyl one was most readily obtained.

β-Naphthylsulphonacetone melts at 130°; the yield was 80 per cent. of the theoretical. Its *oxime* melts at 172°, the yellowish *phenylhydrazone* at 147°; when it is mixed with thiophenol, a little benzene and powdered zinc chloride added, and dry hydrogen chloride passed in, *β-naphthylsulphonacetonephenylmercaptol*, $CH_3\cdot C(SPh)_2\cdot CH_2\cdot SO_2\cdot C_{10}H_7$, melting at 100°, is formed; when its alcoholic solution is saturated with gaseous ammonia, *β-naphthylsulphonacetonamine*,

$$CH_3\cdot C(NH)\cdot CH_2\cdot SO_2\cdot C_{10}H_7,$$

melting at 124°, is formed; with hydrogen cyanide and with sodium hydrogen sulphite, no compounds are formed. *β-Naphthylsulphomonobromacetone* melts at 130—132°; a *dibromo*-compound melting at 155—157° can also be obtained, and it appears that a tetrabromo-derivative is formed as a result of heating on the water bath with excess of bromine in acetic acid solution. *Di-β-naphthylsulphonacetone*, $CO(CH_2\cdot SO_2\cdot C_{10}H_7)_2$, melts at 200°, and forms an *oxime* melting at 116°. *β-naphthylparatolylsulphonacetone*,

$$C_7H_7\cdot SO_2\cdot CH_2\cdot CO\cdot CH_2\cdot SO_2\cdot C_{10}H_{17},$$

melts and decomposes at 185°; the *oxime* melts at 158°, the yellow *phenylhydrazone* at 186°, and the *acetonamine* at 126°. *β-Naphthylphenylsulphonacetone*, $C_6H_5\cdot SO_2\cdot CH_2\cdot CO\cdot CH_2\cdot SO_2\cdot C_{10}H_7$, melts at 144°, the *oxime* at 167°, and the yellowish *phenylhydrazone* at 175°.

By acting on β-naphthylsulphomonobromacetone with sodium phenyl or sodium β-naphthyl sulphides, C_6H_5SNa, &c., *thiophenyl-* and *β-thionaphthyl-β-naphthylsulphonacetones* are obtained,

$$C_6H_5\cdot S\cdot CH_2\cdot CO\cdot CH_2\cdot SO_2\cdot C_{10}H_7,$$

&c.; by hot permanganate solution, these are oxidised to the corresponding disulphones. *a-Naphthylsulphonacetone* melts at 65°, and yields an *oxime*; both substances crystallise with difficulty. C. F. B.

A Menthoglycol. By PHILIPPE BARBIER and GEORGES LESER (*Compt. rend.*, 1897, **124**, 1308—1311).—*Menthoglycol* (*menthanediol*-3 : 8), $CHMe<\begin{matrix}CH_2\cdot CH(OH)\\CH_2\text{——}CH_2\end{matrix}>CH\cdot CMe_2\cdot OH$, is obtained by agitating citronellaldehyde with 10 parts of 5 per cent. sulphuric acid during 12 hours; it is colourless, and almost odourless, crystallising from light petroleum in lustrous, white plates, melting at 81—81·5°. Acetic anhydride at 100° converts it into the *monacetyl* derivative, which boils at 137—138° under a pressure of 10 mm.; at 150°, in presence of fused sodium acetate, the anhydride gives rise to the acetyl derivative of isopulegol. Hydrogen chloride in presence of glacial acetic acid converts the glycol into what appears to be a mixture of two isomerides; the product has the formula $C_{10}H_{18}Cl\cdot OAc$, and boils at 124—125° under a pressure of 10 mm. The relation which the glycol bears to isopulegol is shown by the conversion of the latter into menthoglycol, and also by the fact that isopulegol is another product of the action of sulphuric acid on citronellaldehyde. A third *compound*, having the formula $C_{20}H_{34}O$, has been also isolated from the products of this action; it boils at 185° under a pressure of 10 mm.

The authors ascribe to citronellaldehyde the constitution

$$CH_2{:}CMe\cdot CH_2\cdot CH_2\cdot CH_2\cdot CHMe\cdot CH_2\cdot COH$$

(compare Barbier and Bouveault, Abstr., 1896, i, 492). This view, however, leads them to represent isopulegol by the constitutional formula $CH_2{:}CMe\cdot CH<\begin{matrix}CH(OH)\cdot CH_2\\CH_2\text{——}CH_2\end{matrix}>CHMe$ (compare Tiemann and Schmidt, Abstr., 1896, i, 383). M. O. F.

Compounds of the *iso*-Geranaldehyde (*iso*-Citral) Series: Preparation and Constitution of Ionone. By PHILIPPE BARBIER and LOUIS BOUVEAULT (*Bull. Soc. Chim.*, 1897, [iii], 15, 1002—1008). Compare Abstr., 1894, i, 83).—In attempting to prepare *iso*-geranionitrile according to the instructions of Tiemann and Semmler (*loc. cit.*), the authors have obtained the *hydrate*, $C_{10}H_{15}N,H_2O$, a viscous liquid which boils at 152° under a pressure of 10 mm.; it is not an amide, being converted into *iso*-geranionitrile under the influence of 70 per cent. sulphuric acid at 100°, the nitrile obtained in this way boiling at 97° under a pressure of 10 mm. (compare *loc. cit.*). *iso*-Geranionitrile is prepared by carefully adding geranionitrile to well cooled 70 per cent. sulphuric acid; another *hydrate* of *iso*-geranionitrile can also be formed, being produced by the action of hot, moderately concentrated sulphuric acid on *iso*-geranionitrile, and this compound separates from benzene in colourless crystals melting at 115°. *iso*-Geranionitrile resists the action of alcoholic potash at 100°, and to some extent also when heated with it at 170° under pressure, but a considerable portion under

these conditions yields the *amide*, $C_9H_{15}\cdot CONH_2$, boiling at 208°, under a pressure of 10 mm., and melting at 121°, along with an isomeric *amide* which melts and sublimes at 202°; these compounds, although yielding nitrogen when treated with nitrous acid, have not been yet converted into *iso*-geranic acid.

The authors represent the constitution of geranionitrile and the hydrate by the expression $CMe_2{:}CH\cdot CH_2\cdot CH_2\cdot CMe{:}CH\cdot CN$ (compare *loc. cit.*), and $OH\cdot CMe_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CMe{:}CH\cdot CN$, regarding *iso*-geranionitrile as having the constitution $CH_2{<}{\begin{matrix}CH_2-CMe\\CH_2\cdot CMe_2\end{matrix}}{>}C\cdot CN$; this conclusion is based on the observation that *iso*-geranionitrile yields hydrogen cyanide, acetone, $\alpha\alpha$-dimethylglutaric acid, and $\alpha\alpha$-dimethylsuccinic acid on oxidation.

Ionone is probably a compound of the *iso*-geranaldehyde series, being easily prepared by the action of sulphuric acid on ψ-ionone, the latter substance being produced from geranaldehyde by condensation with acetone (Tiemann and Krüger, Abstr., 1894, i, 82). ψ-Ionone is accordingly represented by the formula

$$CMe_2{:}CH\cdot CH_2\cdot CH_2\cdot CMe{:}CH\cdot CH{:}CH\cdot COMe,$$

ring formation yielding ionone, $CH_2{<}{\begin{matrix}CH_2-CMe\\CH_2\cdot CMe_2\end{matrix}}{>}C\cdot CH{:}CH\cdot COMe$, which is transformed on dehydration into ionene, $\begin{matrix}CH_2-CH_2\cdot C\cdot CH{:}CMe\\ | \qquad\qquad \| \qquad\quad | \\ CH_2\cdot CMe_2\cdot C\cdot CH{:}CH\end{matrix}$ (compare Tiemann and Krüger, *loc. cit.*).

M. O. F.

Isolauronolic Acid. By G. Blanc (*Compt. rend.*, 1897, **124**, 1361—1364).—*iso*-Lauronolic acid dissolves readily in concentrated sulphuric acid, and on warming the solution on the water bath, is converted into sulphocamphylic acid (compare Abstr., 1893, i, 363); Koenigs and Hoerlin (*loc. cit.*) have obtained *iso*-lauronolic acid by the action of superheated steam on sulphocamphylic acid, and the author has prepared it by the action of aluminium chloride on camphoric anhydride (this vol., i, 201). It is noteworthy that, although *iso*-lauronolic acid is unsaturated, the sulphonic derivative has the properties of a saturated compound.

When the chloride of *iso*-lauronolic acid is heated with the sodium derivative of ethylic malonate suspended in toluene, the *compound*, $C_8H_{13}\cdot CO\cdot CH_2\cdot COOEt$, is produced; it is a mobile liquid, of agreeable odour, and boils at 185—190° under a pressure of 17 mm. The substance is very unstable, and an aqueous solution of caustic potash converts it into a gelatinous *compound* which is rapidly converted into potassium *iso*-lauronolate.

iso-*Lauronolylic cyanide*, $C_8H_{13}\cdot CO\cdot CN$, is obtained by heating dry silver cyanide with *iso*-lauronolylic chloride in sealed tubes at 100° during 4 hours; it is a mobile liquid, of penetrating odour, and boils at 120° under a pressure of 23 mm. Hydrolysis regenerates *iso*-lauronolic acid.

iso-*Lauronolonitrile*, $C_8H_{13}\cdot CN$, is formed as a bye-product in preparing the amide if considerable quantities of the acid chloride in ethereal solution are treated with gaseous ammonia, but it is more convenient to dehydrate the amide (this vol., i, 201) with acetic chloride

or phosphorus pentachloride. It is a colourless, mobile liquid, of penetrating odour, and boils at 205° under a pressure of 760 mm.; reduction converts it into a base which will be described subsequently.

M. O. F.

Cochineal Dye. By CARL T. LIEBERMANN and HUGO VOSWINCKEL (*Ber.*, 1897, **30**, 1731—1744. Compare this vol., i, 292).—The authors have shown that the colouring matter of cochineal, when oxidised with potassium persulphate, yields two acids, which they term coccinic and cochinelic acids, provisionally ascribing to these substances the formulæ $C_9H_8O_5$, and $C_{10}H_8O_7$ respectively (*loc. cit.*). Further investigation has established the identity of the former with hydroxyuvitic acid, which most probably has the constitution $OH\cdot C_6H_2Me(COOH)_2$ [$Me : OH : (COOH)_2 = 1 : 3 : 4 : 6$]; moreover, by the action of heat, water and carbonic anhydride have been eliminated from cochinelic acid, which thus gives rise to the anhydride of *β-coccinic acid*, an acid isomeric with hydroxyuvitic acid, having the constitution $OH\cdot C_6H_2Me(COOH)_2$ [$Me : OH : (COOH)_2 = 1 : 3 : 5 : 6$]. These observations, coupled with the fact that tribromocresotic acid, the product of brominating cochinelic acid, yields the cresotic acid melting at 210° when reduced, point to the formula $OH\cdot C_6HMe(COOH)_3$ [$Me : OH : (COOH)_3 = 1 : 3 : 4 : 5 : 6$] for cochinelic acid, which must be therefore regarded as a homohydroxyhemimellitic acid.

Silver cochinelate, containing $1H_2O$, is not insoluble in water, and remains hydrated when heated for some time at 75°. The calcium salt (*loc. cit.*) crystallises in small needles, and retains $7H_2O$ after being dried at 130°, but becomes anhydrous at 180°. The *barium* salt also forms needles, contains $2H_2O$ at 130°, and becomes anhydrous at 180°. The *methylic* salt, obtained from methylic iodide and the silver salt, melts at 78—80°; in agreement with Victor Meyer's generalisation regarding the etherification of the tricarboxylic acids, cochinelic acid, which contains carboxylic groups attached to three neighbouring carbon atoms, does not yield alkylic salts when treated with hydrogen chloride in presence of an alcohol. The *ethylic* salt is a viscous oil, which slowly dissolves in cold, dilute, caustic alkali, acids precipitating the *hydrogen diethylic* salt from the solution; this substance crystallises in colourless needles and scales resembling benzoic acid, and melts at 136—137°. The *acetyl* derivative crystallises from benzene and petroleum in plates, and melts indefinitely at 142—143°.

Tribromocresotic acid develops a yellow, and not reddish-violet coloration with ferric chloride (compare *loc. cit.*); when reduced with sodium amalgam, it yields cresotic acid melting at 210°, passage of carbonic anhydride accelerating the action, and giving rise to a colourless, resinous substance. Cresotic acid is also formed when cochinelic acid is heated with water in sealed tubes at 200—210° for 2—3 hours; if the operation is conducted at 170°, and interrupted after one hour, *α*-coccinic (hydroxyuvitic) acid is produced.

β-Coccinic acid, $OH\cdot C_6H_2Me(COOH)_2$ [$Me:OH:(COOH)_2 = 1:3:5:6$], is very readily soluble in water, and melts at 155—157°; ferric chloride develops a yellowish turbidity, but no red coloration, and the acid gives the fluorescein reaction when fused with resorcinol. The *anhydride* is

obtained by heating cochinelic acid at 250—260° until gas is no longer evolved; it separates from benzene in small nodules, and melts at 166—168°. The *silver* salt is anhydrous.

The authors discuss the constitution of cochineal-carmine, and point out that this substance, which has the formula $C_{11}H_{12}O_6$, may prove to be the hydrindene derivative, $\begin{array}{l}COOH\cdot C_6HMe(OH)\cdot CH\cdot OH \\ \quad\quad\quad\;\, CH(OH)\text{——}CH\cdot OH\end{array}$, or the corresponding derivative of bis-hydrindene, $C_{22}N_{22}O_{12}$ (compare v. Miller and Rohde, Abstr., 1894, i, 94; also Schunck and Marchlewski, Abstr., 1895, i, 67). M. O. F.

Carminic Acid. By WILHELM VON MILLER and GEORG ROHDE (*Ber.*, 1897, **30**, 1759—1766. Compare Abstr., 1894, i, 94; also Schunck and Marchlewski, Abstr., 1895, i, 67).—Carminic acid has been hitherto regarded by the authors as having the constitution of a hexahydroxy-α-methylnaphthalene, but the recognition of a carboxyl group compels them now to modify this view. The empirical formula of the compound is once more thrown in doubt, because the molecular weight is probably that of a substance having the composition $C_{24}H_{22}O_{14}$, or $C_{22}H_{20}O_{13}$ (compare preceding abstract).

The *acetyl* derivative, $C_{24}H_{12}O_{13}Ac_8$(?), is obtained by heating carminic acid with acetic anhydride (10 parts) and a small quantity of zinc chloride or concentrated sulphuric acid until dissolution is complete, the reddish-yellow liquid becoming brownish-red; on pouring the liquid into water, a bluish-yellow precipitate is formed. This is a mixture of acetyl derivatives, and is immediately hydrolysed to carminic acid when treated with cold dilute caustic alkali. The main product crystallises from methylic alcohol in long, bright yellow needles, and melts gradually at 155—165°, whilst the bye-product, which yields the foregoing substance on further acetylation, forms golden-yellow, microscopic needles, and melts, decomposing, at 210°; the latter *compound* gives analytical results which agree with the formula $C_{24}H_{16}O_{14}Ac_6$. It is the discovery that the acetyl derivative is a carboxylic acid which has led the authors to modify their views in the above-mentioned manner.

Carminic acid, in addition to the anilide described by Schunck and Marchlewski (*loc. cit.*), yields an additive *compound*,

$$(C_{12}H_{11}O_7)_2,C_6H_5\cdot NH_2,$$

which crystallises from 50 per cent. alcohol in red needles, and melts and decomposes at 190°. The quinoline additive *compound*,

$$(C_{12}H_{11}O_7)_2,C_9H_7N,$$

forms red scales, and melts and decomposes at about 220°.

M. O. F.

Metallic Compounds of Pyridine and the Electrolysis of Pyridine. By LUDWIG PINCUSSOHN (*Zeit. anorg. Chem.*, 1897, **14**, 379—403).—The paper contains an account of the metallic compounds of pyridine already described.

Lead chloride pyridine, $4PbCl_2,3C_5NH_5$, is obtained by dissolving lead chloride in boiling pyridine. It crystallises in white needles, deliquesces in the air and gives off a strong odour of pyridine. *Lead*

nitrate pyridine, $Pb(NO_3)_2,2C_5NH_5$ and *lead iodide pyridine* are prepared in a similar manner and have similar properties.

Lead chloride pyridine hydrochloride, $2PbCl_2,C_5NH_5,HCl + 2H_2O$, is obtained by saturating an aqueous solution of pyridine hydrochloride with lead chloride and allowing the mixture to crystallise. It crystallises in slender, lustrous, white needles which are quite stable on exposure to the air. The author was unable to obtain the salt,

$$3PbCl_2,4C_5NH_5,HCl,$$

described by Classen and Zahorsky. The salts with *ferric chloride*, $Fe_2Cl_6,3C_5NH_5,HCl + 3H_2O$; *barium chloride*, $(BaCl_2)_3,C_5NH_5,HCl + H_2O$; *magnesium chloride*, and *silver chloride* are also described. With manganous chloride, two salts are obtained. The *salt*, $MnCl_2,2C_5NH_5,HCl$, is formed by saturating an aqueous solution of pyridine hydrochloride with manganous chloride and allowing the solution to crystallise; it separates in yellow crystals, melts at 170—175°, cannot be recrystallised without decomposition, and dissolves to a rose coloured solution in water and alcohol. The *salt*, $MnCl_2,C_5NH_5,HCl$, is obtained by dissolving molecular proportions of pyridine hydrochloride and manganous chloride in water and evaporating the solution on the water bath; it is deposited from alcohol in rose coloured crystals, and can be recrystallised without decomposition.

Silver nitrate pyridine nitrate, $5AgNO_3,3C_5NH_5,HNO_3$, is obtained by evaporating an aqueous solution of silver nitrate and pyridine nitrate on the water bath. It crystallises from alcohol in beautiful, silky needles, is stable on exposure to the air, and when heated in a porcelain crucible gives a beautiful silver mirror. The following nitrates are also described: with *uranium nitrate*, $UrO_2(NO_3)_2,3C_5NH_5,HNO_3 + 2H_2O$; with *copper nitrate*; with *lead nitrate*, $Pb(NO_3)_2,C_5NH_5,HNO_3$; with *cobalt nitrate*, $Co(NO_3)_2,3C_5NH_5,HNO_3$; with *strontium nitrate*, $Sr(NO_3)_2,C_5NH_5,HNO_3$.

The following *sulphates* are also described: *nickel sulphate pyridine sulphate*, $3NiSO_4,2C_5NH_5,H_2SO_4 + 10H_2O$, and the salts of pyridine sulphate with cobalt sulphate, $4CoSO_4,C_5NH_5,H_2SO_4 + 10H_2O$; with zinc sulphate, $3ZnSO_4,2C_2NH_5,H_2SO_4 + 2H_2O$; with ferrous sulphate, $8FeSO_4,C_5NH_5,H_2SO_4 + 3H_2O$; with aluminium sulphate,

$$Al_2(SO_4)_3,4C_5NH_5,H_2SO_4 + 6H_2O,$$

and with copper sulphate, $3CuSO_4,C_5NH_5,H_2SO_4 + 18H_2O$. Double salts with lead sulphate and with barium sulphate could not be obtained. Nearly all the above salts crystallise well, are stable on exposure to the air, and have no odour; whereas the compounds of pyridine with a metallic salt are very unstable and easily lose their pyridine, or the greater part of it, on exposure to the air. The latter salts can also be prepared by dissolving a metallic oxide in an aqueous solution of a pyridine salt, that is, pyridine hydrochloride. Lead chloride pyridine and lead nitrate pyridine have been prepared by this method.

Pyridine phosphate, $C_5NH_5,2H_3PO_4 + H_2O$, is obtained by neutralising phosphoric acid with pyridine, evaporating the mixture to a syrup, and allowing it to remain for some time. It is a white, amorphous mass, cannot be obtained crystalline, has no odour of pyridine, and is fairly stable on exposure to the air.

Pyridine tungstate, $C_5NH_5,2WO_2(OH)_2$, is obtained by mixing aqueous solutions of pyridine sulphate and sodium tungstate. It separates from hot water in microscopic crystals. *Pyridine molybdate*, $C_5NH_5,3MoO_2(OH)_2$, is obtained as a white precipitate by mixing solutions of pyridine sulphate and sodium molybdate. It is easily soluble in hot water, sparingly so in cold water.

The author is unable to confirm the results obtained by Ahrens (this vol., i, 368) in the electrolysis of pyridine. Piperidine is formed under some conditions in very small quantity only, but usually not at all, whereas Ahrens obtained 95 per cent. of the theoretical yield. The brown compound mentioned by Ahrens as being produced at the cathode in two only of his experiments, was obtained by the author in all cases except where a very small current density was employed. A *new base* of the composition C_5NH_7O is also formed at the cathode. It is insoluble in water, alcohol, ether, benzene, chloroform, and pyridine, soluble in a hot solution of pyridine sulphate, and in hot concentrated acids. The hydrochloride yields characteristic double salts with platinic chloride, picric acid, mercuric chloride, and potassium ferrocyanide. E. C. R.

Compounds of Pyridine, Piperidine and Quinoline with Metallic Salts. By RAOUL VARET (*Compt. rend.*, 1897, **124**, 1155—1157).—The general method of preparing the compounds described by the author is to dissolve the metallic salt in hot pyridine, filter out of contact with air, and allow to cool. Cuprous bromide yields green crystals of the composition $Cu_2Br_2,4C_5NH_5$; zinc iodide yields slender, prismatic needles of the compound $ZnI_2,2C_5NH_5$; zinc cyanide yields a gelatinous mass, the composition of which oscillates between $Zn(CN)_2,2C_5NH_5$ and $2Zn(CN)_2,3C_5NH_5$; cadmium bromide at a low temperature yields the compound $CdBr_2,6C_5NH_5$, and when this is dissolved in hot pyridine, the compound $CdBr_2,2C_5NH_5$ separates in long prismatic needles as the liquid cools; nickel bromide yields green crystals of the compound $NiBr_2,2C_5NH_5$ in addition to the compound $NiBr_2,4C_5NH_5$, previously described.

All these compounds are very soluble in hot pyridine; when the crystals are heated pyridine is volatilised.

The author has also prepared compounds of pyridine, piperidine and quinoline with halogen salts of aluminium and iron, with barium, strontium, and calcium iodides, and with manganese bromide and iodide. He has also investigated the action of piperidine on zinc, cadmium, nickel, and cobalt chlorides, bromides, and iodides, and has prepared compounds of quinoline with salts of silver, mercury, copper, &c. These compounds will be described in a subsequent paper. C. H. B.

1-Methylpyrrolidine. By GIACOMO L. CIAMICIAN and ANTONIO PICCININI (*Ber.*, 1897, **30**, 1789—1791).—1-Methylpyrrolidine, obtained by reducing 1-methylpyrroline with hydriodic acid and phosphorus at 250°, appears to be identical in every particular with the base obtained from hygric acid by Liebermann and Cybulski (Abstr., 1895, i, 311). The picrate crystallises in golden-yellow scales, and melts at 218°; the aurochloride forms yellow needles and melts at 218—219°.

M. O. F.

Action of Antipyrine on Trihydric Phenols. By GUSTAVE PATEIN and E. DUFAU (*Bull. Soc. Chim*, 1897, [iii], **15**, 1048—1050. Compare this vol., i, 297 and 375).—*Pyrogallol-antipyrine*,

$$C_6H_3(OH)_3,C_{11}H_{12}N_2O,$$

separates as an oil on mixing concentrated aqueous solutions of antipyrine and pyrogallol; it forms colourless crystals and melts at 77—78°. *Phloroglucinol-antipyrine* melts at 182—184°.

When aqueous solutions of antipyrine and gallic acid are mixed, an oil separates, and soon deposits crystals; the liquid, however, appears to be more in the nature of a solution than a compound, and no evidence of combination has been obtained. M. O. F.

Action of Chloral Hydrate on Phenylhydrazine: Diphenylglyoxazole and its Derivatives. By HENRI E. CAUSSE (*Compt. rend.*, 1897, **124**, 1029—1032).—*Trichlorethylidene-bisphenylhydrazine*, $CCl_3\cdot CH(NH\cdot NHPh)_2$, is a very unstable compound obtained on adding an aqueous solution of chloral hydrate to phenylhydrazine hydrochloride dissolved in water; it forms colourless crystals, but when exposed to air it immediately loses hydrogen chloride and becomes amorphous, ultimately resembling aniline black.

Chlorodiphenylglyoxazole, $NHPh\cdot N<\genfrac{}{}{0pt}{}{CH}{CCl}>N\cdot NHPh$, is prepared by adding chloral hydrate dissolved in water to a solution of phenylhydrazine phosphate in aqueous glycerol (compare Causse, this vol., i, 408); it is a deep red, crystalline powder, insoluble in water, but dissolving in alcohol, ether, and chloroform. It readily loses chlorine under the influence of alkalis.

Hydroxydiphenylglyoxazole, $NHPh\cdot N<\genfrac{}{}{0pt}{}{-CH-}{C(OH)}>N\cdot NHPh$, is obtained by the action of chloral hydrate on phenylhydrazine thiosulphate; it is an orange-coloured, crystalline powder, and melts at 146°. The *barium* derivative forms microscopic, yellow crystals, and the *antimony* derivative, prepared from chloral hydrate and antimony phenylhydrazine tartrate, is scarlet. M. O. F.

Orthamidobenzylamines. IV. By MAX BUSCH (*J. pr. Chem.*, 1897, [ii], **55**, 356—375.)—[With RUD. BIRK and WILHELM LEHMANN.]—*Diorthamidodibenzylamine*, $NH(CH_2\cdot C_6H_4\cdot NH_2)_2$, was prepared by reducing dinitrodibenzylamine (the *hydrochloride* of which melts and decomposes at 236°) with tin and hydrochloric acid; it melts at 71°, and forms a *hydrochloride* (with 3HCl) melting above 280°, and a *tribenzoyl* derivative melting at 218°. When it is heated with carbon bisulphide in the presence of alcoholic potash, *orthamidobenzylthiotetrahydroquinazoline*, $C_6H_4<\genfrac{}{}{0pt}{}{NH\cdot CS}{-CH_2-}>N\cdot CH_2\cdot C_6H_4\cdot NH_2$, is formed, melting at 212°. This can be reduced by sodium, in hot alcoholic solution, to *3-orthamidobenzyltetrahydroquinazoline*, $C_6H_4<\genfrac{}{}{0pt}{}{NH\cdot CH_2}{-CH_2-}>N\cdot CH_2\cdot C_6H_4\cdot NH_2$, (which forms a stable *hydrochloride*, with 1HCl, melting and decomposing at 280—300°, and a yellow *platinochloride* melting above 300°); by diazotisation and subsequent treatment with β-naphthol,

it yields an orange-red azo-dye, *β-naphtholazobenzylthiotetrahydroquinazoline*, melting at 225°. When diamidodibenzylamine is itself diazotised (with 2 mols. of nitrous acid) and then treated with β-naphthol, dark red *β-naphtholorthazobenzyl-β-phenodihydrotriazine*, $C_6H_4<{N:N \atop CH_2}>N\cdot CH_2\cdot C_6H_4\cdot N_2\cdot C_{10}H_6\cdot OH$, melting and decomposing at 185°, is formed. It condenses readily with aldehydes, $R\cdot COH$, at the ordinary temperature, forming compounds of the type

$$C_6H_4<{NH\cdot CHR \atop CH_2}>N\cdot CH_2\cdot C_6H_4\cdot NH_2;$$

benzaldehyde yields *2-phenyl-3-orthamidobenzyltetrahydroquinazoline* melting at 140°; salicylaldehyde and parahydroxybenzaldehyde yield the similar *2-orthohydroxyphenyl* and *2-parahydroxyphenyl* compounds, which melt at 166° and 90° respectively.

[With Rud. Birk.]—When orthomethoxyphenylthiotetrahydroquinazoline is heated for 5 hours in a sealed tube at 140—145° with twenty times its weight of hydriodic acid (sp. gr. 1·96) and a little acetic acid, a substance is obtained that melts at 160—161°, and forms an orange *platinochloride* melting above 280°; it is doubtless a thiazole derivative, $C_6H_4<{N{=}C\cdot S \atop CH_2\cdot N}>C_6H_4$.

When orthamidobenzylamine derivatives of the type

$$NHR\cdot CH_2\cdot C_6H_4\cdot NH_2$$

are treated with 2 mols. of nitrous acid, compounds of the general formula $NO\cdot NR\cdot CH_2\cdot C_6H_4\cdot N:NCl$ are formed, which yield azo-dyes with β-naphthol in the usual manner. *Ortho-β-naphtholazobenzylphenylnitrosamine* is orange-red, melts at 155°, and exchanges the NO group for H when it is heated with alcoholic hydrochloric acid, yielding *β-naphtholazobenzylaniline*, which is red, with a yellow shimmer, and melts at about 176°. *β-Naphtholazobenzylorthotolylnitrosamine* melts at 147—148°, and resembles the phenyl compound in colour and reactions.

C. F. B.

Solubility of Ecgonine. By William Oechsner de Coninck (*Compt. rend.*, 1897, **124**, 1159—1160).—The author has determined the solubility of ecgonine in the ordinary media; the results are stated in c.c. of the solvent required to dissolve 1 gram of the alkaloid. Distilled water, 4·6 at 17°; ethylic alcohol (95°), 67 at 17°; ethylic acetate, 77 at 20·6°; methylic alcohol ("rectified"), 18·5 at 19·2°; ethylic alcohol ("rectified") 17 at 19·6°; ethylic alcohol (71°), 21·3 at 19·8°; paraldehyde, 133·4 at 17·7°. The alkaloid is insoluble in the following media: ether, acetone, petroleum (b. p. 32—50° and b. p. 50—65°), chloroform, bromoform, benzene, toluene, isobutyric alcohol, ethylenic bromide, carbon bisulphide, carbon tetrachloride, and French turpentine.

M. O. F.

Organic Chemistry.

Action of Nickel on Ethylene: Synthesis of Ethane. By Paul Sabatier and Jean Baptiste Senderens (*Compt. rend.*, 1897, **124**, 1358—1361. Compare this volume, i, 305).—When ethylene is passed with moderate rapidity over nickel previously reduced in hydrogen, and heated at a temperature not exceeding 325°, the issuing gas is a mixture of about 10 volumes of hydrogen with about 60 volumes of ethane and 30 volumes of methane. At higher temperatures, the proportion of ethane diminishes, and only traces remain when the temperature approaches a dull red heat. It would seem that the first change is the decomposition of ethylene into carbon and ethane, the latter, at higher temperatures, being converted into carbon and methane, the methane ultimately splitting up into carbon and hydrogen. Direct experiments show that ethane is partially decomposed by nickel at 325°, and that pure methane is also decomposed, especially above 390°. A long column of nickel has practically the same effect on ethane as an increase of temperature, and even at 325° ethylene can be converted almost completely into methane, mixed with a small quantity of hydrogen.

In order to prepare ethane, a mixture of hydrogen with an excess of ethylene is passed over reduced nickel, heated at a temperature not exceeding 150°, and the process may go on for several hours with a comparatively small quantity of nickel. The process has, therefore, the advantage over Wilde's method, in which platinum is used but has to be continually renewed. Reduced cobalt, iron, or copper cannot be substituted for the nickel.

Under similar conditions, ethylene shows no tendency to combine with either water or ammonia. C. H. B.

Action of Acetylene on Silver Nitrate. By R. Chavastelon (*Compt. rend.*, 1897, **124**, 1364—1366).—When acetylene is passed into an aqueous solution of silver nitrate, a white precipitate is formed, and the acidity of the liquid increases somewhat rapidly until all the silver nitrate has been precipitated, and afterwards it increases slowly. In presence of an excess of the silver salt, the quantity of free nitric acid is always higher than that which corresponds with the quantity of silver nitrate that has disappeared. The acetylene compound combines with some silver nitrate as such, and the quantity of silver nitrate decomposed is twice as great as that which enters into combination in this way. Experiments with definite volumes of acetylene, combined with an analysis of the precipitate, show that the first compound formed has the composition $C_2Ag_2,AgNO_3$. It is decomposed by the prolonged action of acetylene, or by hot ammonia solution, the silver nitrate being decomposed or dissolved, whilst silver carbide, C_2Ag_2, is left. The action of acetylene on an ammoniacal solution of the silver salt yields silver carbide at once, as Keiser has stated. These results are analogous to those obtained by

Bruylants and Béhal with hydrocarbons derived from acetylene by substitution. C. H. B.

Compounds of Hydrocarbons with Metallic Salts. By KARL A. HOFMANN and F. KÜSPERT (*Zeit. anorg. Chem.*, 1897, **15**, 204—207).—The *compound*, $(Cu_2Cl_2)_3,C_2H_2$, obtained by the action of pure acetylene on a solution of anhydrous cupric chloride in absolute alcohol, crystallises in colourless needles; the same compound is obtained when methylic alcohol is employed, but the substance then crystallises in forms resembling those of Karlsbad feldspar. When treated with water, it is converted into copper acetylide, whilst with hydrochloric acid it is decomposed into acetylene and cuprous chloride. The reduction of the cupric chloride is due to the action of the acetylene, for by mixing the alcoholic filtrate from the crystals with water, and extracting the mixture with ether, an oily liquid is obtained which yields acetylene when treated with zinc. The compound is not explosive. If 75 per cent. alcohol is employed in the preparation, a reddish-brown powder is obtained which is slightly explosive, and, when treated with hydrochloric acid, yields acetylene, cuprous chloride, and a black residue.

The *compound*, $Ni(CN)_2,NH_3,C_6H_6$, which is formed in small quantities by the action of coal gas on a mixture of nickel hydroxide and ammonia, is easily obtained by shaking a solution of freshly-precipitated nickel cyanide in strong ammonia with benzene. It is a bluish-white powder; when heated, it becomes green, then brown, and finally black, and a very voluminous carbonaceous residue is formed, ammonium cyanide volatilising. Although, when boiled with water, or with a solution of potassium cyanide, the benzene is liberated, it is in very stable combination; no dissociation takes place when the compound is kept in a vacuum, and the benzene is only partially removed by prolonged washing with ether. E. C. R.

Aluminium Alkoxides. By HOMER WINTHROP HILLYER (*Amer. Chem. J.*, 1897, **19**, 597—603. Compare this vol., i, 235).—In the preparation of these substances, platinic chloride can be used, as well as mercuric and stannic chlorides; when stannic chloride is used, the absence of water is essential. Ferric, and even aluminium, chloride can be used, but, in these cases, heat is necessary in order to start the reaction. Finally, if a little alcoholic hydrogen chloride be added to alcohol standing over aluminium cuttings, a reaction will occur.

Aluminium methoxide and *isopropoxide* were prepared, but they crumbled to a dark powder when heated, and gave no distillate. *Aluminium propoxide* boils at 255° under 15 mm. pressure, and resembles commercial glucose in appearance. *Aluminium amyloxide* is yellow, and boils at 291° under 12 mm. pressure. Stannic chloride appears to have been used in the preparation of these substances. C. F. B.

Interaction of Glycerol and Acetic Acid. By ADOLF C. GEITEL (*J. pr. Chem.*, 1897, [ii], **55**, 417—429).—Triacetin is undoubtedly formed when glycerol is treated with acetic acid, the best method being to heat 200 grams of dry glycerol with 500 grams of acetic acid for

8 hours, and after distilling off the acetic acid under diminished pressure, to add 150 grams more of acid, and continue the heating for 16 hours longer. Triacetin, which is best isolated from the product by diluting with water and extracting with ether, is a colourless liquid, only slightly soluble in water, 100 c.c. of its aqueous solution saturated at 15° containing 7·17 grams of the compound. It has a sp. gr. = 1·1605 at 15°/15°, and distils without decomposition at 172—172·5° under a pressure of 40 mm.

On concentrating the aqueous solution left after extraction with ether, and fractionating the product under a pressure of 40 mm., diacetin passed over between 175—176°; it is a soluble, colourless liquid, having a sp. gr. = 1·1769 at 15°/15°.

In order to isolate the monacetin formed in the reaction, the aqueous solution, after the extraction of the triacetin, was extracted for 8 hours with ether at 34—35° in an extracting apparatus for liquids; the later extracts were collected separately, diluted with an equal volume of water, and, after being extracted with hot benzene, were concentrated. The monacetin was thus obtained as a thick, colourless liquid of sp. gr. = 1·2212 at 15°/15°.

By prolonging the ether extraction still further, *monacetyldiglycerol*, $C_3H_5(OH)_2\cdot O\cdot C_3H_5(OAc)\cdot OH$, was obtained. It is a colourless liquid having a sp. gr. = 1·2323 at 15°/15°; this compound is formed in larger quantities when the conditions of the experiment are such that the monacetin first formed remains in contact with the glycerol for some time. Diacetyldiglycide was also separated from the monacetin on fractionation; moreover, triacetyldiglycerol was obtained from the first ether extract, in the separation of the monacetin. J. F. T.

Molecular Volumes of Crystallised Carbohydrates. By JOSEPH PIONCHON (*Compt. rend.*, 1897, **124**, 1523—1524).—Playfair and Joule found that the molecular volumes of saccharose and lactose at 0° are identical with the volume of the water, as ice, of which they contain the elements. The author has determined the specific gravities at 0° of other carbohydrates with the following results:

Sugar.	Sp. gr. at 0°.	Molecular volume.	Volume of water as ice.	Difference between observed and calculated sp. gr.
Xylose	1·535	97·7	97·99	0·005
Glucose	1·538	117·0	117·6	0·008
Levulose	1·555	115·7	117·6	0·025
Saccharose	1·59	215·1	215·6	0·004
Lactose ($+H_2O$)	1·53	235·2	235·2	0·000
Melezitose ($+2H_2O$)	1·5565	347·7	352·8	0·026
Raffinose ($+5H_2O$)	1·465	405·4	411·58	0·022

Even where the divergence from the numbers required by Joule and Playfair's law is greatest, it does not amount to 2 per cent.

Adopting for carbon the volume 9·9, hydrogen 6·2, and oxygen 5·5, 2·3, or 0·4, according as it is acidic, alcoholic, or aldehydic, the formula for the volume of a solid carbohydrate, $C_\alpha H_\beta O_\gamma$, becomes

$$V_m = 9{\cdot}9\alpha + 6{\cdot}2\beta + 5{\cdot}5\gamma + 2{\cdot}3\gamma' + 0{\cdot}4\gamma'' + 24{\cdot}6,$$

and this agrees very closely with the observed values in the case of anhydrous carbohydrates. In the case of lactose, melezitose, or raffinose, which contain water of crystallisation, it is necessary to add a fourth value of the oxygen actually present as water, the latter being regarded as ice. When this is done, the observed and calculated values are practically identical. C. H. B.

The Glycogen of Fungi and Yeasts. By G. CLAUTRIAU (*Bied. Centr.*, 1897, **26**, 423—424; from *D. Bierbrauer.*, 1896, Heft. 9, 131).—Glycogen from animal and vegetable sources behaved analogously in all the experiments made. They are ternary, non-nitrogenous compounds, which are not in combination with any mineral substance. Their pseudo-solutions are precipitated by alcohol, acetic acid, and certain salts. They are all strongly dextrorotatory: D = 189·18°. The action of diastase or dilute acids on glycogens of different origin give rise to the same compounds.

Yeast-glycogen gives a brownish-violet coloration with iodine, whilst the other glycogens are coloured brownish-red. Whilst the latter become almost colourless at 58—60°, yeast-glycogen retains a brown tint at that temperature, but becomes colourless at 72—73°; on cooling, the colour returns.

Another slight difference observed between the various glycogens was their behaviour when dried; in one case, the glycogen was obtained in light flakes, in another case, in a compact condition. The opalescence of yeast-glycogen is less than that of the others.

The results do not decide whether there is only one glycogen. It is suggested that the slight differences observed may be due to polymerisation, or that there may be isomerides. N. H. J. M.

A Peculiarity of Soluble Starch. By MARTINUS WILLEM BEYERINCK (*Bied. Centr.*, 1897, **26**, 430; from *Centr. Bakt.*, 1896, **2**, 697).—Soluble starch retains the properties and structure of starch grains, but dissolves in all proportions in boiling water, from which it separates, on cooling, in an amorphous form. The solutions cannot be mixed with gelatin solutions, but form an emulsion when shaken. With a 20 per cent. solution of starch and a 5 per cent. gelatin solution, a plate of starch is formed, with enclosed drops of gelatin; the latter in turn enclose extremely finely divided drops of starch. When the amount of gelatin is increased, so many gelatin drops are formed that they touch one another on solidifying, and flatten, so that artificial cell-tissues can be produced, the walls of which consist of starch, the contents being gelatin. With a still greater amount of gelatin, the starch separates as drops, which, however, do not show double refraction. If salt is added, a certain amount of starch dissolves in the gelatin. Glycerol (20 per cent. or more) seems to produce a complete solution.

When undisturbed, the specifically heavier starch solution effects a separation of the constituents. With gelatin or agar, with inulin, or gum arabic or dextrin, this was not observed, so that it seems to be a question of a specific property of the starch in relation to gelatin. The amount of water may be varied considerably without materially affecting the result. N. H. J. M.

Condensation of Guanidine and of Carbamide with Ethylic Oxalate. By R. MÜLLER (*J. pr. Chem.*, **55**, 505—507).—Guanidine and ethylic oxalate yield *ethylic dioxalguanidine*,

$$NH:C[N:C(COOEt)\cdot CH_2\cdot COOEt]_2,$$

a substance which crystallises in plates melting at 147°. With carbamide, two substances can be obtained, the one when 2 mols. of the oxalate combine with 1 mol. of carbamide is *ethylic dioxalcarbamide*, $CO[N:C(COOEt)\cdot CH_2\cdot COOEt]_2$, crystallising in white prisms which melt at 104°, and the other when 1 mol. of the oxalate combines with 2 mols. of carbamide, the product being *ethylic uracilcarboxylate*, $CO<\begin{matrix}NH\cdot C(COOEt)\\NH\text{———}CO\end{matrix}>CH$, crystallising in needles and melting at 189°.

J. F. T.

Behaviour of Chloral Hydrate with Ammonium Sulphide. By JOSEPH LESINSKY and CHARLES GUNDLICH (*Amer. Chem. J.*, 1897, **19**, 603—606).—When 2 grams of chloral hydrate are dissolved in 25 c.c. of water, and 10 c.c. of the solution rapidly mixed with 5 c.c. of yellow ammonium sulphide in a narrow beaker, after a certain lapse of time (which is always the same for the same temperature), a precipitate is suddenly formed. At 1°, 20°, 45°, and 65° respectively, the separation takes place after 44, 19, 8, and 3 seconds. The precipitate is pink to yellowish-brown, but its nature has not yet been determined. Butylchloral (crotonchloral) gives a similar reaction, but the precipitate is lemon-yellow, and is formed in 2 or 3 seconds. C. F. B.

Condensation Products of Isovaleraldehyde. By ALBERT REYCHLER (*Bull. Soc. Chim.*, 1896, [iii], **15**, 970—973).—Isovaleraldehyde was heated for several hours with dry potassium carbonate, and the product distilled under reduced pressure. After several fractionations, a substance was obtained boiling at 140—145° (20 mm.), and having the formula $C_{10}H_{20}O_2$; its sp. gr. at 22° = 0·8962, and its index of refraction at 22° = 1·42995. It reduces an ammoniacal solution of silver nitrate only after the addition of a caustic alkali, and does not react either with hydroxylamine or with phenylhydrazine. The author is studying the constitution of this substance.

From the higher fractions obtained in the distillation of the products of the action of chromic acid mixture on amylic alcohol, a fraction boiling at 137—141° (20 mm.) was obtained. The formula of this substance is $C_{15}H_{32}O_2$, its sp. gr. = 0·835 at 22°, and its index of refraction = 1·42289 at 22°. It is probably identical with the amylidenediamylic ether, $C_4H_9\cdot CH(O\cdot C_5H_{11})_2$, prepared by Alsberg.

A. C. C.

Reduction of αβ-Unsaturated Ketones. By CARL D. HARRIES and FRIEDRICH HÜBNER (*Annalen*, 1897, **296**, 295—328).—Deoxymesitylic oxide (*Δ¹-cyclopentene-2-methyl-4-dimethyl-5-dimethyl-1-ethanone*), $\begin{matrix}CMe_2\text{———}CH_2\\CMe_2\cdot C(COMe)\end{matrix}>CMe$, is the compound first obtained by von Baeyer on reducing mesitylic oxide, and subsequently investigated by Claisen (compare also Harries and Eschenbach, Abstr., 1896, i, 306, and Kerp, Abstr., 1896, i, 448). When the reduction is carried out by means of sodium amalgam, the portion of the product which boils at

210—230° yields two isomeric oximes, but only one derivative is obtained when aluminium amalgam is employed.

The *a-oxime* is the sole product of the action of hydroxylamine on the oil obtained by reducing mesitylic oxide with aluminium amalgam; it separates from alcohol in rhombic, hemimorphic crystals, and melts at 156—157°. The *hydrochloride* crystallises from alcohol in six-sided leaflets containing $1H_2O$, and melts at 124—125°.

The *β-oxime* is obtained along with the foregoing when the product of reduction of mesitylic oxide with sodium amalgam is treated with hydroxylamine; the substance also melts at 156—157°, but the crystals are of different habit, although belonging to the rhombic system. The *hydrochloride* melts at 105—106°.

Acetamidopentamethylcyclopentene, $\begin{array}{l}CMe_2\text{———}CH_2\\ | \\ CMe_2\cdot C(NHAc)\end{array}\!\!>\!CMe$, obtained by heating the oxime with concentrated mineral acid in a reflux apparatus, is a colourless oil which boils at 89—91° under a pressure of 10—12 mm. The *hydriodide* melts at 170°, and the *picrate* crystallises from alcohol in pale yellow, six-sided plates melting at 179—180°; the *aurochloride* and *platinochloride* are also crystalline.

Pentamethyl-Δ^1-cyclopentenol, $\begin{array}{l}CMe_2\text{—}CH_2\\ | \\ CMe_2\cdot C(OH)\end{array}\!\!>\!CMe$, is a bye-product of the action of mineral acids on the oxime, and is isolated by submitting the product to distillation in a current of steam; it is a colourless, refractive oil, having the odour of camphor, and boils at 60—62° and 93—95° under pressures of 8 mm. and 34 mm. respectively. Oxidation with chromic acid in glacial acetic acid gives rise to tetramethylsuccinic acid.

The *hydrochloride* of amidoethylpentamethylcyclopentane,

$$\begin{array}{l}CMe_2\text{——————}CH_2\\ | \\ CMe_2\cdot CH(CHMe\cdot NH_2)\end{array}\!\!>\!CHMe,HCl,$$

is obtained on reducing the *a*-oxime with sodium and absolute alcohol, and melts at 214—215°. The *hydrobromide* melts at 187—188°, and the *platinochloride* begins to decompose at 100°.

Deoxyphorone, $\begin{array}{l}CMe_2\text{——————}CH_2\\ | \\ CMe_2\cdot C(CO\cdot CH\!:\!CMe_2)\end{array}\!\!>\!C\cdot CH\!:\!CMe_2$, is prepared by reducing phorone with sodium amalgam, and melts at 108—109°; Claisen obtained it by means of zinc dust and sulphuric acid. The hydroxylamine *compound* crystallises in aggregates of needles and melts at 133—134°; the substance is not an oxime, and reduces Fehling's solution when moderately heated.

Deoxyphorone pinacone, $C_{36}H_{58}O_2$, prepared by heating deoxyphorone with zinc dust and sulphuric acid in a reflux apparatus, crystallises from benzene in needles, and melts at 194—195°. The solution in concentrated sulphuric acid is dark red.

The *compound*, $C_{15}H_{24}O$, is produced along with deoxyphorone, when phorone is reduced; it boils at 137—139° under a pressure of 8—10 mm.

The secondary *alcohol* of benzylacetophenone, $CH_2Ph\cdot CH_2\cdot CHPh\cdot OH$, is obtained on reducing benzylideneacetophenone in alcoholic solution with sodium amalgam; it boils at 330—332° under atmospheric pres-

sure. The *compound*, $\begin{matrix}CHPh\cdot CH_2\cdot CPh\cdot OH \\ CHPh\cdot CH_2\cdot CPh\cdot OH\end{matrix}$, is produced under the same conditions, and after crystallisation from xylene melts at 210—211°; reduction with hydriodic acid and phosphorus in glacial acetic acid solution converts it into the *compound*, $C_{30}H_{28}O$, which sinters at 175° and melts at 182°.

It has been observed by Schneidewind that benzylacetophenone is the chief product of reducing benzylideneacetophenone with zinc dust and glacial acetic acid. The *compound* $C_{30}H_{26}O_2$ is produced along with it, and crystallises from xylene in slender needles melting at 270°.

M. O. F.

Action of Nitric Peroxide on Isonitrosoketones. By GIACOMO PONZIO (*Gazzetta*, 1897, **27**, i, 271—279).—Nitric peroxide acts on aliphatic isonitrosoketones of the composition R·CO·C(NOH)R′ much as nitric acid acts on ketones, with formation of diketones, dinitroketones, and varying proportions of dinitro-hydrocarbons and aliphatic acids. The first reaction which occurs is in accordance with the equation $2R\cdot CO\cdot C(NOH)R' + 2N_2O_4 = 2R\cdot CO\cdot C(NO_2)_2R' + N_2O + H_2O$; the dinitro-ketones thus formed are characterised, as has been shown by Fileti and Ponzio (Abstr., 1895, i, 499; this vol., i, 317), by hydrolysing in accordance with the equation $CMe(NO_2)_2\cdot CO\cdot CH_2\cdot CHMe_2 + H_2O = CHMe(NO_2)_2 + CHMe_2\cdot CH_2\cdot COOH$. Isonitrosoacetone, which, according to these equations, should yield acetyldinitromethane and methylglyoxal when treated with nitric peroxide, behaves exceptionally, and, without evolution of gas, gives a white, viscid mass, which inflames spontaneously when left, even in contact with water.

The general method of operating is to add the proper quantity of a dry ethereal solution of nitric peroxide to a cooled solution of the isonitrosoketone in anhydrous ether; the evolution of gas ceases after several hours, and the product is then washed with water, dried with sodium sulphate, and the ether distilled off, when a yellow oil is left. The oil thus obtained from isonitrosodiethylketone is washed with sodium hydrogen carbonate solution, which removes acetylpropionyl and dinitroethane; the residue consists of impure *propionyldinitroethane*, $CMe(NO_2)_2\cdot CO\cdot CH_2Me$, which crystallises in lustrous laminæ melting at 43—44°, is very volatile, and possesses a camphor-like odour. It is very readily hydrolysed by water, yielding propionic acid and dinitroethane.

Isonitrosoethyl isopropyl ketone, $CMe(NOH)\cdot CO\cdot CHMe_2$, which is easily prepared by Claisen and Manasse's method (Abstr., 1889, 584), crystallises in lustrous needles melting at 93—94°, and is very volatile in a current of steam. On treatment with hydroxylamine, it yields *acetylisobutyryldioxime*, $CMe(NOH)\cdot C(NOH)\cdot CHMe_2$, which crystallises in long needles melting at 155—156°. The oil obtained on treating the ketone with nitric peroxide solidifies slowly, depositing *isobutyryldinitroethane*, $CMe(NO_2)_2\cdot CO\cdot CHMe_2$, which crystallises in lustrous laminæ melting at 58°, and is also obtained on treating ethyl isopropyl ketone with nitric acid; the oil separated from the dinitro-compound contains acetylisobutyryl and dinitroethane.

Isonitrosoethyl isobutyl ketone, $CMe(NOH)\cdot CO\cdot CH_2\cdot CHMe_2$, prepared

by treating ethyl isobutyl ketone with amylic nitrite, crystallises in flattened, lustrous needles melting at 64—65°; the *dioxime* obtained from it melts at 171—172°. *βa-Acetylisovalerylphenylhydrazoxime*,

$$CMe(NOH)\cdot C(N_2HPh)\cdot CH_2\cdot CHMe_2,$$

is prepared by heating the ketone with phenylhydrazine in alcoholic solution; it crystallises in almost colourless prisms melting at 127—128°, and on boiling its alcoholic solution with fuming hydrochloric acid yields *β-acetylisovalerylphenylhydrazone*,

$$CMeO\cdot C(N_2HPh)\cdot CH_2\cdot CHMe_2,$$

which crystallises in yellow needles melting at 94°, and gives an *osazone* melting at 115—116°.

The oily product obtained by treating isonitrosoethyl isobutyl ketone with nitric peroxide contains, in addition to dinitroethane and acetylisovaleryl, *isovaleryldinitroethane*, $CMe(NO_2)_2\cdot CO\cdot CH_2\cdot CHMe_2$, which crystallises in broad laminæ melting at 65—66°, and may be also prepared by the action of nitric acid on ethyl isobutyl ketone.

On treating isonitrosomethyl ethyl ketone with nitric peroxide as described above, an oily *substance*, probably acetyldinitroethane, $CMeAc(NO_2)_2$, is obtained. W. J. P.

Tropeines of the Triacetonamine Series. By CARL D. HARRIES (*Annalen*, 1897, **296**, 328—343. Compare this vol., i, 293).—*av-Dimethylvinyldiacetonalkammonium iodide*, $NMe_2I\langle\begin{matrix}CHMe\cdot CH_2 \\ OH \\ CMe_2-CH_2\end{matrix}\rangle CH$, is obtained by the action of methylic iodide on α-vinyldiacetonalkamine (this vol., i, 295), dissolved in methylic alcohol, at the ordinary temperature; it crystallises from alcohol in plates, and decomposes about 270°. A portion of the original substance resists the action of methylic iodide, and after removing the foregoing salt, may be precipitated from the ethereal solution by means of light petroleum, in which it is but sparingly soluble; on evaporating the filtrate with hydrobromic acid, the *hydrobromide* of *av*-methylvinyldiacetonalkamine is obtained, and crystallises from absolute alcohol in six-sided plates. The *hydrate*, produced on treating the aqueous solution of the hydrobromide with caustic soda, melts at 39—40°, being precipitated in lustrous scales on adding light petroleum to the solution in benzene.

av-Methylvinyldiacetonalkamine, $NMe\langle\begin{matrix}CHMe\cdot CH_2 \\ OH \\ CMe_2-CH_2\end{matrix}\rangle CH$, is obtained as an oil on exposing the hydrate in the desiccator, and boils at 225—226° under a pressure of 744 mm.; the *aurochloride* crystallises from dilute hydrochloric acid in large plates, and the *platinochloride* forms microscopic prisms.

Application of the mandelic acid reaction to the substituted vinyldiacetonalkamines has led to results comparable with the observations of Liebermann and Limpach in connection with ψ-tropine (Abstr., 1892, 891); homatropine, and the corresponding mandelic derivative of the labile (β-)vinyldiacetonalkamine are definitely crystalline, whilst ψ-homatropine and the mandelic derivative of *av*-methylvinyldiacetonalkamine are oils.

a-Phenylglycolyl-v-methylvinyldiacetonalkamine,

$C_9H_{18}NO \cdot CO \cdot CHPh \cdot OH$,

is obtained by heating the methylated base dissolved in hydrochloric acid with mandelic acid on the water bath; it is an oil which does not dissolve readily in water, and has a strongly alkaline action on turmeric. When the alkaloid is evaporated in a porcelain dish with a few drops of fuming nitric acid, and the deep brown residue treated with alcoholic potash, a persistent orange coloration is developed. The *aurochloride* forms microscopic needles, but the salts generally are not characteristic. The alkaloid is very feebly anæsthetic, and does not induce mydriasis.

βv-Dimethylvinyldiacetonalkammonium iodide is obtained by the action of methylic iodide on β-vinyldiacetonalkamine. *βv-Methylvinyldiacetonalkamine*, $NMe<\substack{CHMe \cdot CH_2 \\ CMe_2—CH_2}>CH \cdot OH$, is produced along with it, and after crystallisation from light petroleum melts at 70—72°, and boils at 220° under a pressure of 744 mm.; treatment with a boiling solution of sodium amyloxide in amylic alcohol for 20 hours converts it into the stable modification. The *hydrochloride* is crystalline, the *aurochloride* forms prisms, and the *platinochloride* also crystallises.

β-Phenylglycolyl-v-methylvinyldiacetonalkamine crystallises from light petroleum in small, six-sided prisms melting at 113°; evaporation with fuming nitric acid, followed by treatment with alcoholic potash, develops a reddish-yellow coloration. The *hydrochloride* is a very hygroscopic micro-crystalline powder, and the *picrate* forms nodules; the *aurochloride* crystallises in golden-yellow plates, sinters at 150°, and melts at 158—159°, whilst the *platinochloride* forms oblique tabular crystals. The alkaloid induces mydriasis in rabbits and men, the maximum effect in the human subject being observed after the lapse of 40 minutes. M. O. F.

Electrolysis of Trichloracetic Acid. By KARL ELBS and K. KRATZ (*J. pr. Chem.*, **55**, 502—505).—Trichloromethylic trichloracetate is formed on electrolysing either sodium trichloracetate or the zinc salt, and consists of white crystals melting at 34°; it is slowly decomposed by water, with formation of chloral and phosgene.

J. F. T.

Behaviour of Thioacetic Acid towards Salt Solutions. By N. TARUGI (*Gazzetta*, 1897, **27**, i, 316—328).—The black precipitate obtained with thioacetic acid and acid solutions of bismuth salts is always bismuth trisulphide, Bi_2S_3. *Bismuth thioacetate*, $Bi(COSMe)_3$, is deposited in long, transparent prisms, melting at 85°, on allowing a solution of bismuth hydroxide in excess of thioacetic acid to evaporate spontaneously. When warmed, in presence of air, with a small quantity of water, the new salt decomposes in accordance with the equation $2Bi(COSMe)_3 + H_2O + O = BiS(COSMe)_3 + BiO(COOMe) + 2HCOSMe$; the *compound* of the composition $BiS(COSMe)_3$ is a red, amorphous powder insoluble in carbon bisulphide. On adding much water to bismuth thioacetate and then boiling, the following reaction occurs: $Bi(COSMe)_3 + 2H_2O = BiS(COSMe) + 2MeCOOH + H_2S$, and the *compound* of the composition BiS(COSMe) separates as a dark-red

powder. Ammonia, soda, sodium carbonate, hydrochloric acid and the alkaline sulphides convert bismuth thioacetate into the trisulphide. Cold concentrated sulphuric acid acts on the thioacetate in accordance with the equation $3Bi(COSMe)_3 + 4H_2SO_4 = Bi_2(SO_4)_3 + (COSMe)BiSO_4 + 8HCOSMe$, and the double *salt* of the composition $(COSMe)BiSO_4$ is deposited as a red powder; hot sulphuric acid converts the thioacetate into bismuth trisulphide. When dry bismuth thioacetate is heated, it first melts, and then decomposes in accordance with the equation $2Bi(COSMe)_3 = Bi_2S_3 + 3SAc_2$, thioacetic anhydride distilling.

On treating the compound of the composition $(COSMe)_3BiS$, with concentrated sulphuric acid, reaction occurs with evolution of heat, in accordance with the following equation: $(COSMe)_3BiS + H_2SO_4 = H_2S + (COSMe)_3BiSO_4$; the new *compound*, $(COSMe)_3BiSO_4$, is brown, and must be prepared in an atmosphere of some inert gas, such as carbonic anhydride. The compound of the composition $(COSMe)BiS$ reacts with concentrated sulphuric acid in accordance with the equation $(COSMe)BiS + H_2SO_4 = H_2S + (COSMe)BiSO_4$.

Bismuth tri-iodide, BiI_3, reacts with thioacetic acid in the cold, with formation of Muir and Eagles' bismuth sulphiodide (Trans., 1895, 90), in accordance with the following equation, $BiI_3 + H\cdot COSMe + H_2O = BiSI + MeCOOH + 2HI$. Iodine in carbon bisulphide solution converts bismuth thioacetate into a red, amorphous *substance* of the composition $(COSMe)BiI_2$. On treating bismuth potassium iodide with iodine and thioacetic acid in carbon bisulphide solution, a yellow, amorphous *substance* of the composition $(COSMe)_2BiI$ is obtained.

Some of the salts described above afford the first examples of quinquivalent bismuth amongst aliphatic compounds. W. J. P.

Isolauronolic Acid. By G. BLANC (*Compt. rend.*, 1897, **124**, 624—626. Compare this vol., i, 538).—When isolauronolic chloride (2 mols.) is treated with zinc-methyl (1 mol.) in the presence of anhydrous ether, the *ketone*, $C_{10}H_{16}O$, is formed. It is a colourless, mobile liquid having a powerful camphor-like odour, is insoluble in water, but soluble in all the ordinary organic solvents. It boils at 200—202°, has a sp. gr. $= 0.9404$ at 14°, and an index of refraction $= 1.474$ at 15°. It distils readily with steam. The *oxime*, $C_{10}H_{16}:NOH$, forms large, transparent, colourless, rhombic crystals melting at 64—65° and boiling at 140° (13 mm.). It is odourless. The *semicarbazone*, $C_{10}H_{16}:N\cdot NH\cdot CO\cdot NH_2$, occurs either as slightly yellow, leaf-like crystals or as fine needles melting at 49°. It is very soluble in ether and light petroleum, less soluble in alcohol. The *phenylhydrazone*, $C_{10}H_{16}:N\cdot NHPh$, is a viscous, yellow liquid boiling at 185—190° (13 mm.).

When the ketone is subjected to the action of nascent hydrogen in ethereal solution and the products of the reaction distilled under reduced pressure, two compounds are obtained, namely, an *alcohol*, $C_{10}H_{18}O$, and a substance having the formula $C_{20}H_{34}O_2$, probably a pinacone. The alcohol is a colourless, mobile liquid having a penetrating odour somewhat resembling that of the ketone; it boils at 205°, and is insoluble in water, but soluble in the ordinary organic solvents. The corresponding *chloride* and *acetate* can be obtained from it. The compound $C_{20}H_{34}O_2$ remains behind after distilling off the alcohol under reduced pressure;

when recrystallised from dilute alcohol, it melts at 120° and is but slightly soluble in alcohol, ether, or light petroleum. On distillation, it undergoes decomposition into the alcohol and the ketone.

A. C. C.

Composition of Some Oil Seeds. By ALEXANDRE HÉBERT (*Bull. Soc. Chim.*, 1896, [iii], **15**, 935—941).—The author describes the examination of three seeds not previously studied, two of which come from the French Congo, whilst the third is obtained from a plant growing in San Salvador. The first seed described is known in the Congo by the name of *I'Sano* or *Unguecko*, and is obtained from a large tree belonging to the Olacineæ family. The decorticated seeds contain 37 per cent. of husk, the analysis of which is given, and 63 per cent. of kernel. The dried kernels yielded 60 per cent. of their weight of fat and oil. An analysis of the extracted residue shows that it contains 33·12 per cent. of proteids, and it would therefore be of value as a cattle food. The oil, which is of a reddish colour and has a sp. gr. = 0·973 at 23°, is viscous, very slightly soluble in 90 per cent. alcohol, and has strong drying properties. With monhydrated sulphuric acid, a rise of temperature of 117° is produced. On saponification and acidification with sulphuric acid, it yields 86 per cent. of brown liquid fatty acids, the lead salts of which are entirely soluble in ether. Fractional precipitation with baryta indicated the presence of three acids, the first being probably identical with oleic acid, the second with linoleic acid, whilst the third consists of a new unsaturated acid of the formula $C_{14}H_{20}O_2$, to which the name *isanic acid* is given (see Abstr., 1896, i, 638).

The second seed studied by the author is known as *Mohamba*, and in many respects resembles the preceding. It contains 35 per cent. of husk (of which an analysis is given) and 65 per cent. of kernel, yielding 12 per cent. of fat and oil. The oil is yellow and has a sp. gr. = 0·915 at 23°. With monhydrated sulphuric acid, it produces a rise of temperature of 55°, and yields 90 per cent. of liquid, insoluble fatty acids, the lead salts of which are completely soluble in ether. The mixed fatty acids, after standing for some time, deposit a white acid, soluble in alcohol and ether, from which it crystallises in plates melting at 34—35°. It unites with approximately the same amount of bromine as oleic acid, and appears to belong to the series $C_nH_{2n-2}O_2$, but does not correspond with any known acid. The liquid from which this solid separates consists of oleic acid.

The third seed is known as *Aceituno*, and is the product of the wild olive tree of Central America. The decorticated seeds yield 64 per cent. of husk and 34 per cent. of kernel. The latter, after extraction with light petroleum, yielded a residue containing a large proportion of tannin and of dextrose, but free from starch. The fat occurs as a yellow mass melting at 30°, which, on saponification and acidification with sulphuric acid, yields more than 90 per cent. of white, solid, fatty acids melting at 48—49°. Of these, about one-half consist of saturated and one-half of unsaturated acids, the former melting at 54—55°. By fractional precipitation with barium chloride, three barium salts were obtained from the mixed saturated acids, yielding acids melting at 58—59°, 44°, and 38° respectively.

A. C. C.

Some Malonic Acid Derivatives.—By RICHARD S. CURTISS (*Amer. Chem. J.*, 1897, **19**, 691—701. Compare Bischoff, this vol., i, 267).—When ethylic bromomalonate, $CHBr(COOEt)_2$ (1 mol.), is allowed to remain at the ordinary temperature with aniline (3 mols.), *ethylic anilidomalonate*, $NHPh \cdot CH(COOEt)_2$, is formed; this crystallises in greenish-white, monoclinic prisms and melts at 44—45°. When heated with mercuric oxide and light petroleum at 95—100°, it is oxidised to *ethylic dianilidomalonate*, $(NHPh)_2C(COOEt)_2$, which is also formed when ethylic dibromomalonate (1 mol.) is left in contact with aniline (5 mols.); this substance melts at 117—118°, and distils with but little decomposition.

When ethylic dibromomalonate, mixed with a little alcohol, is dropped into alcoholic sodium ethoxide kept at 48—50°, ethylic diethoxymalonate is formed, together with some ethylic carbonate; if the temperature is kept at 10—15°, diethoxymalonate is formed in less amount, and none is obtained if 4 mols. of sodium ethoxide (instead of 2) are used per mol. of ethylic dibromomalonate; evidence was obtained in all cases of the formation of substances with the reactions of bromoform and of aldehyde, and a certain amount of the ethylic salts became hydrolysed, and some carbonic anhydride was usually evolved. If the sodium ethoxide is dropped into the ethylic dibromomalonate (at 30—40°), ethylic ethylenetetracarboxylate, $C_2(COOEt)_4$, is formed, together with a little ethylic carbonate, but no diethoxymalonate could be isolated from the product. C. F. B.

Derivatives of Bromomaleic and Chloromaleic Acid-aldehydes. By HENRY BARKER HILL and EUGENE T. ALLEN (*Amer. Chem. J.*, 1897, **19**, 650—667).—When pyromucic acid (1 mol.) is suspended in water and bromine (3 mols.) added gradually, the mixture being cooled and shaken, 2 mols. of bromine react readily, but the other one only slowly. The product is finally extracted with ether, and the residue from this extract treated with hydroxylamine hydrochloride, when *bromomaleic acid-aldoxime*, $NOH\!:\!CH \cdot C_2HBr \cdot COOH$, is formed, and may be purified from mucobromic acid and mucobromoxime by warming for a short time with a little water; the acid-aldehyde itself could not be isolated. This acid-aldoxime melts with explosive decomposition at about 143°; its *barium* salt, with $4H_2O$, and anhydrous *lead* and *silver* salts were prepared; its *methylic* salt, obtained by boiling a methyl-alcoholic solution of the acid after adding a very little strong sulphuric acid, melts at 152—153°. The acid-aldoxime itself is converted by heating with water at 110° into ammonium hydrogen bromomaleate; when it is dissolved in strong sulphuric acid and the solution poured gradually into carefully cooled water, it yields the *acid-aldoxime anhydride*, $C_4H_2BrNO_2$, which melts at 83° when pure; when this substance is heated above its melting point, it undergoes a molecular transformation into bromomaleimide, which cannot be obtained by heating the acid-aldoxime itself. When the acid-aldoxime is heated with acetic acid to which 20 per cent. of acetic anhydride has been added, and the mixture is then saturated with gaseous hydrogen chloride, chlorobromosuccinic acid, $C_4H_4BrClO_4$, is formed. If it is dissolved in methylic alcohol, and the solution saturated with gaseous hydrogen

chloride or bromide, the methylic salts of *chlorobromo-* and *dibromo-succinic acid-aldoximes*, $C_4H_4BrCl(or\ Br_2)NO_3Me$, melting at 167—168° and 161—162°, are respectively formed. With dry bromine in chloroform solution at 75—80°, it forms *tribromosuccinic acid-aldoxime*, $C_4H_4Br_3NO_3$, melting at 133°; this loses hydrogen bromide and carbonic anhydride when it is warmed with water, forming *dibromacraldoxime*, $C_3H_3Br_2NO$, which melts at 104° or lower, and yields dibromacraldehyde when boiled with dilute hydrochloric acid, for the oily product, although it could not be obtained pure, is oxidised by silver oxide to $\alpha\beta$-dibromacrylic acid.

An analogous set of chlorine compounds was prepared by similar methods, starting with pyromucic acid (1 mol.), which was suspended in cooled hydrochloric acid, an amount of manganese dioxide just necessary to liberate 3 mols. of chlorine being then added gradually. *Chloromaleic acid-aldoxime* melts and decomposes at 150°; the *anhydride* melts at 58°, and the *methylic* salt at 130°. The *methylic* salts of *dichlorosuccinic* and *bromochlorosuccinic acid-aldoximes* melt at 135° and 145° respectively; the second must be isomeric with the chlorobromo-compound described above.

Incidentally, *mucochloroxime anhydride* was prepared from the oxime by treatment with sulphuric or hydrochloric acid; it melts at 76—77°.

C. F. B.

Absorption of Oxygen by Tetrabromofurfuran. By HENRY A. TORREY (*Amer. Chem. J.*, 1897, **19**, 668—671. Compare Hill and Hartshorn, Abstr., 1885, 762).—When tetrabromofurfuran, $\begin{matrix} CBr{:}CBr \\ | \\ CBr{:}CBr \end{matrix}\!\!>\!O$, is exposed to direct sunlight for 6—7 hours in a flask through which dry oxygen is passed slowly, it becomes oxidised to a yellow substance which solidifies completely after a time, and which is doubtless dibromomaleic bromide, $\begin{matrix} CBr{\cdot}CBr_2 \\ \| \\ CBr\text{—}CO \end{matrix}\!\!>\!O$, for it forms dibromomaleic and hydrobromic acids when it is boiled with water. The gain in weight is only 80—85 per cent. of the theoretical, but this is due to the formation of some dibromomaleic anhydride from the bromide first formed; in fact, if the reaction is prolonged beyond 6—7 hours, a loss of weight is manifested, and bromine is evolved.

C. F. B.

Exchange of Bromine for Chlorine in Aromatic Compounds. By RUDOLF WEGSCHEIDER (*Monatsh.*, 1897, **18**, 329—346).—When concentrated hydrochloric acid acts on *s*-tribromaniline at a temperature of 200°, the latter is converted into *s*-trichloraniline. The conversion is, however, incomplete, on account of the hydrobromic acid formed during the process, which produces the opposite reaction, namely, exchange of chlorine for bromine. This explanation is supported by the fact that, when concentrated hydrobromic acid acts on *s*-trichloraniline, the tribromo-compound is formed, a second reaction taking place at the same time, namely, the substitution of bromine for hydrogen. As the reaction is carried out in sealed tubes, presumably the oxygen of the enclosed air acts on the hydrobromic acid, forming free bromine, which then replaces hydrogen. At a higher temperature, it should

therefore be possible to replace more than three hydrogen atoms in aniline by bromine.

In hydrolysing *s*-tribromobenzonitrile containing chloro-*s*-tribromobenzene, concentrated hydrochloric acid was used. As *s*-tribromobenzoic acid was produced, it follows that there is no appreciable exchange of bromine for chlorine when either of these substances is acted on by hydrochloric acid.

Tribromaniline is acted on by cuprous chloride, reduction taking place, aniline and monobromo- and dibromo-derivatives of aniline being formed. Exchange of bromine for chlorine takes place only to a small extent.

The author discusses the theory of these and similar reactions at some length, and points out that Köhnlein's propositions (*Annalen*, **225**, 194) regarding the influence of the metal combined with a halogen on the exchange of a halogen element between an inorganic and an organic halogen compound do not hold good in general, but must be provisionally confined to the exchange of halogen with organic compounds possessing no basic character, and in which the halogen enters an open chain.

A. W. C.

Some Derivatives of Anethoil. By GEORGES DARZENS (*Compt. rend.*, 1897, **124**, 563—565).—*Anethoil dichloride* is prepared by slowly pouring a solution of chlorine (1 mol.) in carbon tetrachloride into a well cooled solution of anethoil (1 mol.) in three times its weight of the same solvent. After distilling off the carbon tetrachloride under reduced pressure, the dichloride is obtained as a mobile, yellow liquid which, on distillation, breaks up into hydrogen chloride, and *monochloranethoil*, $OMe\cdot C_6H_4\cdot C_3H_4Cl$ [1 : 4], boiling at 258°, melting at 6°, and having a sp. gr. = 1·135 at 0°. It has an odour of the oil of anise, and is identical with the derivative obtained by Ladenburg by the action of phosphorus pentachloride on anethoil. *Monochloranethoil dichloride* is obtained by treating the preceding compound with a solution of chlorine in carbon tetrachloride. It is a white, crystalline substance melting at 35° and soluble in all the ordinary organic solvents. *Monochloranethoil dibromide*, prepared by treating monochloranethoil with a solution of bromine in carbon tetrachloride, is a white, crystalline substance melting at 45°. The odour of anethoil is not modified by the substitution of chlorine for hydrogen in the side-chain.

A. C. C.

Trichlorotrimethylphloroglucinol and Trichlorotrimethylpyrogallol. By PIETRO BARTOLOTTI (*Gazzetta*, 1897, **27**, i, 289—291).—*Trichlorotrimethylphloroglucinol*, $OMe\cdot C{<}{\begin{matrix}CCl\cdot C(OMe)\\ CCl{:}C(OMe)\end{matrix}}{>}CCl$, is prepared by passing dry chlorine through a hot acetic acid solution of trimethylphloroglucinol, precipitating the solution with water, and distilling the deposit in a current of steam; it crystallises in thin, white needles melting at 130—131°, and is identical with the product obtained by Ciamician and Silber on treating methylhydrocotoin or methylprotocotoin with phosphorus pentachloride. A mixture of chlorinated products is obtained by chlorinating trimethylphloroglucinol in the cold.

Trichlorotrimethylpyrogallol, $OMe\cdot C \begin{matrix} \diagup C(OMe)\cdot CCl \diagdown \\ \diagdown C(OMe):CCl \diagup \end{matrix} CCl$, obtained by the direct chlorination of trimethylpyrogallol in cold acetic acid solution, is purified by the method used above for its isomeride; it separates from alcohol in beautiful crystals melting at 54°.

W. J. P.

Halogen Addition-products of the Anilides. By HENRY LORD WHEELER, BAYARD BARNES, and JULIUS HOWARD PRATT (*Amer. Chem. J.*, 1897, **19**, 672—682. Compare Abstr., 1896, 1367.)—Ammonium tri-iodide, NH_4I,I_2, obtained by evaporating a solution of the calculated quantity of iodine in concentrated aqueous ammonium iodide, crystallises in rhombic prisms [$a:b:c = 0.6950:1:1.1415$], and is isomorphous with the corresponding trihaloids of potassium, rubidium, and cæsium. The trihaloids of the anilides are quite dissimilar, crystallising in the monoclinic or triclinic system. The hydrogen-haloids were prepared by passing the dry halogen haloid into a solution of the anilide in ethylic acetate, chloroform, or benzene; by dissolving them in hot glacial acetic acid, adding the calculated quantity of iodine or bromine, and allowing the solution to cool, or to evaporate spontaneously, crystals of the perhaloids are obtained; these are more or less red in colour, and are darker the more iodine they contain. The following compounds were prepared: $NHAcPh,HCl,I_2$. $NHAcPh,HBr$. $NHAcPh,HBr,I_2$; triclinic [$a:b:c = 0.5707:1:1.2005$; $\alpha = 89° 26'$, $\beta = 132° 20'$, $\gamma = 83° 16'$]. $(NHAcPh)_2,HI$. $(NHAcPh)_2,HI,I_2$; triclinic [$\alpha = 102° 56'$, $\beta = 104° 34'$, $\gamma = 113° 2'$]. $(C_6H_4Br\cdot NHAc)_2,HCl$ [1 : 4]. $(C_6H_4Br\cdot NHAc)_2,HCl,I_2$. $(C_6H_4Br\cdot NHAc)_2,HBr,I_2$. $(C_6H_4Br\cdot NHAc)_2,HI$. $(C_6H_4Br\cdot NHAc)_2,HI,I_2$; triclinic (? *mono*-clinic) [$a:b:c = 1.853:1:3.015$; $\beta = 79° \frac{1}{2}'$]. $(C_6H_4Br\cdot NHAc)_2,HI,I_4$. $NO_2\cdot C_6H_4\cdot NMeAc,HBr$ [1 : 3]. $(NO_2\cdot C_6H_4\cdot NMeAc)_2,HBr,Br_2$. $(NO_2\cdot C_6H_4\cdot NMeAc)_2,HBr,I_4$. $(NHPh\cdot CHO)_2,HCl$. $(NHPh\cdot CHO)_2,HI$. $NHPh\cdot CHO,HI$. $(NO_2\cdot C_6H_4\cdot NHAc)_2,HCl$ [1:3].

C. F. B.

Mercurioaniline. By LEONE PESCI (*Gazzetta*, 1897, **27**, i, 567—574).—The author has previously obtained mercurioaniline (Abstr., 1892, 1448), and also paramercuriodiphenylenemercuriodiamine (Abstr., 1894, i, 248). Mercurioaniline reacts with sodium thiosulphate, potassium iodide, ammonium bromide, and carbon bisulphide in accordance with the equations $(NHPh)_2Hg + Na_2S_2O_3 + 2H_2O = HgS_2O_3 + 2NH_2Ph + 2NaOH$. $(NHPh)_2Hg + 2KI + 2H_2O = HgI_2 + 2NH_2Ph + 2KOH$. $(NHPh)_2Hg + 2NH_4Br = HgBr_2 + 2NH_2Ph + 2NH_3$. $(NHPh)_2Hg + CS_2 = HgS + (NHPh)_2CS$. On comparing these reactions with those of paramercuriodiphenylenemercuriodiamine (Piccinini, Abstr., 1895, i, 358), it will be seen that, in the latter case, the reagent acts, just as in the above reactions, on the mercury attached to nitrogen, whilst the mercury attached to the phenylene nucleus is not attacked and gives paramercurioaniline; the latter has the constitution $Hg(C_6H_4NH_2)_2$, and is an isomeride of mercurioaniline, $Hg(NHPh)_2$, containing mercury attached to nitrogen only. Mercurioaniline is con-

verted by acids into aniline and a mercuric salt; by treatment with mercuric acetate, it gives the *diacetate* of paramercuriodiphenylene-mercuriodiamine, $Hg{<}\substack{C_6H_4\cdot NH(OAc)\\ C_6H_4\cdot NH(OAc)}{>}Hg$, which crystallises in yellow, transparent needles soluble in acetic acid. W. J. P.

Preparation of 1 : 2 : 3-Metaxylidine. By ARTURO MIOLATI and ALFREDO LOTTI (*Gazzetta*, 1897, **27**, i, 293—299).—Luhmann (*Annalen*, 1860, **113**, 274,) and Bussenius and Eisenstuck (*Annalen*, **114**, 156), by treating metaxylene with fuming nitric acid, obtained the following trinitroxylene, $CH{<}\substack{C(NO_2)\cdot CMe\\ C(NO_2):CMe}{>}C\cdot NO_2$, which, when reduced with hydrogen sulphide in ammonia solution, gives a mixture of a monamine with the diamine, $CH{<}\substack{C(NH_2)\cdot CMe\\ C(NH_2):CMe}{>}C\cdot NO_2$; the latter may be converted into 2-nitrometaxylene, either by passing nitrous fumes into its boiling alcoholic solution, or by adding cooled ethylic nitrite to a concentrated solution of its sulphate in dilute alcohol and then gradually raising the mixture to the boiling point. The nitroxylene, when reduced by iron and acetic acid, gives 1 : 2 : 3-metaxylidine boiling at 210—212°, as stated by Nölting and Forel (Abstr., 1886, 58).

Paratolilsuccinimide, when treated with fuming nitric acid, yields a *compound* which crystallises in yellow laminæ melting at 137°; its decomposition by potash shows it to have the constitution

$$CMe{<}\substack{C(NO_2)\cdot CH\\ CH{=\!=\!=}CH}{>}C\cdot N{<}\substack{CO\cdot CH_2\\ |\\ CO\cdot CH_2}.$$

The succinimide of the composition $CH{<}\substack{CMe\cdot CH\\ CMe:CH}{>}C\cdot N{<}\substack{CO\cdot CH_2\\ |\\ CO\cdot CH_2}$, on nitration, gives two products, one of which, on hydrolysis, yields a previously unknown nitroxylidine. W. J. P.

Combination of Metallic Salts with the Homologues of Aniline and their Isomerides. By D. TOMBECK (*Compt. rend.*, 1897, **124**, 1531—1534. Compare this vol., i, 463).—When alcoholic solutions of toluidine and of the halogen salts of zinc or cadmium are mixed, compounds of the type $M''X_2,2C_7H_7\cdot NH_2$ are formed. The zinc salts crystallise in small, white needles, and all the compounds alter rapidly and become discoloured when exposed to air; when gently heated, toluidine is liberated. Cupric chloride, bromide, and iodide form very unstable compounds analogous to the aniline compound $CuCl_2,2NH_2Ph$ described by Destrem.

Xylidine yields similar compounds with the chlorides, bromides, and iodides of zinc and cadmium, and their formation is accompanied by a distinct development of heat.

Picoline behaves similarly; the compounds are of the same type, and form colourless crystals. Lutidine and collidine likewise yield analogous compounds which crystallise well.

All these compounds are but slightly soluble in water; the organic base is slowly liberated at the ordinary temperature and more rapidly on heating. They have a distinct vapour pressure at the ordinary

temperature, and when thrown on water show movements similar to those of camphor.

Bases derived from aniline by substitution behave in the same way as the homologues and their isomerides. C. H. B.

Nitrosodiphenylmethylamine. By CH. CLOËZ (*Compt. rend.*, 1897, **124**, 898—901).—The ease with which nitrosodimethylaniline can be prepared from dimethylaniline led the author to endeavour to prepare a dinitroso-derivative from diphenylmethylamine by the action of nitrous anhydride. This was, however, found to be impossible, the mononitroso-derivative alone being always formed. A solution of sodium nitrite (15 grams) in water (70 grams) was added drop by drop to a solution of diphenylmethylamine (40 grams) in hydrochloric acid solution of sp. gr. = 1·165 (200 grams) cooled to $-10°$. After some time, crystals of the hydrochloride of nitrosodiphenylmethylamine separated, from which the base was prepared by dissolving in water and precipitating with sodium carbonate. It crystallises from methylic alcohol in fine green plates melting at 44°, and is very stable. With dimethylmetamidophenol, the hydrochloride of this base forms a fine blue-colouring matter, which is readily fixed on cotton mordanted with tannin. When two parts of nitrosodiphenylmethylamine are treated with three parts of gallic acid, a product is obtained which is soluble in sodium carbonate solution and which dyes wool and silk a violet-blue. It is also fixed by cotton treated with metallic mordants or with tannin.

Sulphonic Derivative of Diphenylmethylamine, $NMePh\cdot C_6H_4\cdot SO_3H$.—185 grams of the base is heated for 10 hours at 160° with 100 grams of ordinary sulphuric acid. At the end of this time, the mixture is treated with a solution of caustic soda, filtered, evaporated to dryness, and the dry residue extracted with boiling alcohol. On evaporation, a crystalline mass of the sodium salt of the above sulphonic acid is obtained; it is very soluble in alcohol and in water, from which it crystallises in small, granular masses consisting of microscopic needles. The acid itself is very soluble in alcohol and in water, but almost insoluble in solutions of hydrochloric acid, strong or dilute. It could not be obtained in a state of purity. On treating a mixture of the sodium salt and sodium nitrite in molecular proportion with hydrochloric acid, a nitroso-derivative is formed. With dimethylmetamidophenol, this nitroso-compound yields a blue colouring matter, and with gallic acid a bluish-violet colouring matter which readily dyes wool, the tint produced resembling certain of the indulines. A. C. C.

Combination of Phenylhydrazine with Metallic Bromides. By JOSEPH MOITESSIER (*Compt. rend.*, 1897, **124**, 1306—1308).—Compounds of phenylhydrazine with metallic bromides are obtained by mixing alcoholic or aqueous solutions of the two substances. Zinc bromide yields $ZnBr_2,2N_2H_3Ph$, which forms anhydrous, white, rectangular lamellæ. Cadmium bromide forms an analogous compound which crystallises in long, quadrangular lamellæ, likewise anhydrous. The magnesium compound is analogous in composition, and crystallises in a similar form. Nickel and cobalt bromides behave similarly, and

the iodides of the metals of the magnesium group likewise combine with phenylhydrazine.

Solutions of the compounds give the reactions of the metallic bromides and phenylhydrazine. C. H. B.

Combination of Phenylhydrazine with Metallic Iodides. By JOSEPH MOITESSIER (*Compt. rend.*, 1897, **124**, 1529—1531).—The compounds described are obtained by adding phenylhydrazine to an alcoholic solution of the particular iodide. Zinc iodide yields the compound $ZnI_2,2NHPh·NH_2$, which crystallises in prisms and elongated rhomboidal lamellæ, and melts at about 175°. In presence of excess of phenylhydrazine, a second compound, $ZnI_2,5NHPh·NH_2$, is formed, and crystallises in white prisms and quadrangular lamellæ; this melts at about 70°, decomposes at about 90°, and is soluble in water and organic solvents. The cadmium compound, $CdI_2,2NHPh·NH_2$, forms minute needles, and the manganous compound is similar in composition and crystalline form; both decompose before melting. The cadmium compound is only slightly soluble in water and cold alcohol, and is insoluble in chloroform; the manganese compound is very soluble in water or alcohol, but quite insoluble in ether or chloroform. The nickel compound, $NiI_2,6NHPh·NH_2$, forms microscopic lamellæ which decompose below 100° and are soluble in water or alcohol, especially when heated, but are only slightly soluble in ether and chloroform.

All these compounds lose phenylhydrazine when heated; if heated strongly in presence of air, they lose iodine also, and a residue of metallic oxide is left. Their solutions give the reactions of phenylhydrazine and the particular iodide. (Compare preceding abstract). Nitrates of the metals of the magnesium series form similar compounds. C. H. B.

Final Contribution to the Question of the Diazo-isomerism. By CHRISTIAN WILHELM BLOMSTRAND (*J. pr. Chem.*, **55**, 481—501).—Polemical matter relating to the Hantzsch-Bamberger controversy.

Action of Paradiazotoluene Nitrate and Sulphate on Methylic Alcohol. By WILLIAM E. CHAMBERLAIN (*Amer. Chem. J.*, 1897, **19**, 531—547. Compare Remsen and Dashiell, Abstr., 1893, i, 325).—The action of methylic alcohol on a paradiazotoluene salt, $C_6H_4Me·N_2X$, may, of course, yield either paramethoxytoluene, $C_6H_4Me·OMe$, or toluene, C_6H_5Me (the alcohol acting as a reducing agent), or both; nitrophenols are also obtained when the diazo-nitrate is used. The yield of the methoxy-compound is greater when the sulphate is used, and greater also when the reaction is carried out under diminished pressure. The following table shows the variety of conditions under which the reaction was effected, and gives the yields of the products in percentages of the theoretical :—

	Nitrate.		Sulphate.	
	Methoxy-toluene.	Toluene.	Methoxy-toluene.	Toluene.
With alcohol, ordinary pressure	29	trace	66	trace
,, diminished ,,	22	10	77	trace
,, increased ,,	39	—	61	trace
With NaOMe	—	36	—	32
With alcohol and KOH	—	44	—	59
,, K_2CO_3	—	53	—	44
,, zinc dust	—	*	—	46
,, zinc oxide	17	22	20	48

* No record ; about the same as the sulphate.

The diminution or increment of the pressure was 500 mm., as compared with the atmospheric pressure. The weight of alcohol used varied from about $2\frac{1}{2}$ to 4 times the weight of the diazo-salt, whilst the weights of sodium (to make NaOMe), KOH, and K_2CO_3 added varied from 6—7, 10—12, and 27—13 per cent. of the alcohol respectively. Heat was used to promote the reaction when necessary; it is interesting to notice that potassium hydroxide, in solution in methylic alcohol, only acts very slowly on the diazo-salt at the ordinary temperature. No diphenyl was obtained in any case (Beeson, Abstr., 1894, i, 329).

The action of dilute nitric acid on paramethoxytoluene yields dinitrocresol melting at 80·5°. This makes it probable that, when nitrophenols are obtained by the reaction of diazo-nitrates with alcohol, these products result from the hydrolysis of alkoxy-compounds first formed, the introduction of nitro-groups taking place at the same time.

C. F. B.

Reaction of Nitrodiazobenzene and Diazobenzoic Acid Salts with Methylic Alcohol. By GEORGE F. WEIDA (*Amer. Chem. J.*, 1897, **19**, 547—561. Compare Remsen and Graham, Abstr., 1889, 975).—The reaction was carried out by heating the diazo-salts on the water bath with 5 to 10 times their amount of methylic alcohol in a reflux apparatus, carefully regulating the temperature at first, and heating finally to 100°. With orthonitrodiazobenzene sulphate, the only product that could be detected was nitrobenzene, and the yield was 87 per cent. of the theoretical. Metanitrodiazobenzene nitrate yields nitrobenzene (51 per cent.) and a little metanitranisoil (metanitromethoxybenzene). Paranitrodiazobenzene nitrate yields both nitrobenzene (47—40 per cent.) and paranitranisoil (8—17 per cent.).

Ortho-, meta-, and para-diazobenzoic acid sulphates, and also the ortho- and para-nitrates, when heated with methylic alcohol, yield the corresponding methylic methoxybenzoates as the chief products. The ortho-nitrate yields also some asymmetrical nitrosalicylic acid [1 : 2 : 4], and the ortho-sulphate yields some methylic benzoate. It is remarkable that the meta-salt yields no benzoate, for it is known to

yield ethylic benzoate when heated with ethylic alcohol. In the case of the para-nitrate, some free methoxybenzoic acid was obtained.

C. F. B.

Action of Methylic Alcohol on Orthodiazotoluene Sulphate. By WILLIAM BROMWELL (*Amer. Chem. J.*, 1897, **19**, 561—577. Compare Remsen and Orndorff, Abstr., 1888, 268).—Orthodiazotoluene sulphate is decomposed by methylic alcohol, both at the ordinary temperature and on the water bath; the product is almost entirely orthomethoxytoluene, $OMe\cdot C_6H_4\cdot CH_3$, only a trace of toluene being formed. Orthomethoxytoluene is oxidised by permanganate to orthomethoxybenzoic acid, $OMe\cdot C_6H_4\cdot COOH$, and when sulphonated with concentrated sulphuric acid at the ordinary temperature, it yields but one derivative, a *mono*sulphonic acid, $OMe\cdot C_6H_3(SO_3H)\cdot CH_3$; this melts at 212°; the *sodium* salt, with $5\frac{1}{2}H_2O$; *potassium* (from alcohol with $\frac{1}{2}H_2O$); *calcium*, with $9H_2O$; *barium* (from dilute solutions in shining transparent plates with $2H_2O$, from concentrated solutions in white irregular opaque crystals with H_2O); *magnesium*, with $5\frac{1}{2}H_2O$; *zinc*, with $6\frac{1}{2}H_2O$; *lead*, with $6H_2O$; and *copper*, with $6H_2O$, salts were prepared, and so were the *sulphonic chloride* and *sulphonamide*. The sulphonamide melts at 137°, and is oxidised by permanganate to *orthomethoxysulphaminebenzoic acid*, $OMe\cdot C_6H_3(SO_2\cdot NH_2)\cdot COOH$, which melts at 211°; no satisfactory result was obtained when this acid was fused with potassium hydroxide (compare Walker, this vol., i, 569).

Other interesting observations are that the nitrate of orthodiazotoluene is dangerously explosive, and that the substance sold in the State of New York as "Columbian spirit" is methylic alcohol, containing a little water, but otherwise quite pure. C. F. B.

Rearrangement of Oximido-derivatives. By ERNST OTTO BECKMANN [and K. SANDEL] (*Annalen*, 1897, **296**, 279—294. Compare Abstr., 1893, i, 474).—The existence of an unstable intermediate compound arising from the action of phosphoric chloride on α-benzilmonoxime has been already indicated (*loc. cit.*); this substance, which behaves in accordance with the constitutional formula, $CPhCl\colon N\cdot COPh$, has now been isolated.

Benzoylbenzimide chloride, $\begin{array}{c}N\cdot COPh\\ \|\\ Ph\cdot C\cdot Cl\end{array}$, is obtained by dissolving α-benzilmonoxime in anhydrous ether and treating the carefully cooled solution with phosphorus pentachloride; if the liquid is not cooled with ice, dibenzamide, ammonia, and benzoic acid are the products. This chloride, which crystallises from light petroleum and melts at 84°, gradually undergoes spontaneous change, yielding benzoic chloride and dibenzamide. When treated with dilute hydrochloric acid at 70—80°, it is scarcely changed at first, but if the liquid is boiled in a reflux apparatus, complete hydrolysis takes place; water produces the same effect, but the substance crystallises from absolute alcohol. The *benzoyl* derivative of γ-benzilmonoxime is obtained as a bye-product when benzoylbenzimide chloride is crystallised from absolute alcohol; it melts at 137°, and yields γ-benzilmonoxime when treated with alcoholic potash. Alkalis, alkali carbonates, carbamide, and moist silver oxide give rise to benzonitrile, whilst hydroxylamine

converts the chloride into dibenzenylazoxime. When ammonia is passed into the benzene solution, benzoylbenzamidine, NH:CPh·NH·COPh, is produced; this substance is identical with the amidine obtained by Pinner from benzonitrile and sulphuric acid.

Benzoylphenylbenzamidine, NPh:CPh·NH·COPh, is obtained by adding aniline to a solution of the chloride in absolute alcohol, and after crystallisation from ether melts at 143°; cold hydrochloric acid resolves the substance into dibenzamide and aniline, and hot water produces the same effect, but the compound resists the action of alkalis. Hydroxylamine liberates aniline, and gives rise to dibenzenylazoxime.

Benzoylbenzylbenzamidine, CH_2Ph·N:CPh·NH·COPh, produced by the action of benzylamine on the chloride dissolved in ether, melts at 147°. Secondary bases do not yield amidines, but give rise to benzo nitrile and benzoic acid.

Hydrazinebenzoylbenzamidine, NH_2·N:CPh·NH·COPh, is prepared from benzoylbenzamide chloride and hydrazine, and after crystallisation from alcohol, melts at 189°. Compared with the foregoing amidine, it is a remarkably stable substance. Hot concentrated hydrochloric acid dissolves it slowly, but without effecting hydrolysis, and it is equally indifferent towards concentrated alkalis; it also resists the action of oxidising and reducing agents. The *hydrochloride* melts at 220—223°; the *phenylsulphone* derivative is obtained by agitation with benzenesulphonic chloride.

Phenylhydrazinebenzoylbenzamidine, NHPh·N:CPh·NH·COPh, obtained when the chloride is gently heated with alcohol and phenylhydrazine, melts at 105°; it forms a *hydrochloride* and a *phenylsulphone* derivative.

Benzoylphenylmethylbenzamidine, NMePh·N:CPh·NH·COPh, is produced by the action of phenylmethylhydrazine on the chloride, and melts at 125°. It is less stable than the hydrazine and phenylhydrazine derivatives, yielding ammonia, benzoic acid, and methylaniline when treated with boiling dilute hydrochloric acid; it resists the action of alkalis.

The foregoing amidines are also produced when benzoylbenzamidine is heated with the corresponding base. M. O. F.

The Difference between Ethers and Salts, considered in relation to the Constitution of the Rosanilines. By AUGUSTE ROSENSTIEHL (*Bull. Soc. Chim.*, 1895, [iii], **15**, 952—959).—The author dissents from the view expressed by Tortelli (Abstr., 1895, i, 540) that, because the rosanilines react readily with certain reagents in aqueous solution, they are to be regarded as salts rather than ethers, silver nitrate, for instance, bringing about the precipitation of the whole of the chlorine in the hydrochloride, whilst the addition of barium chloride to a solution of the sulphate causes the precipitation of the theoretical quantity of barium sulphate. It is pointed out that no sharp distinction, based upon the ease with which their electro-negative elements or radicles are removed by certain reagents, can be drawn between *salts* on the one hand, and *ethers* on the other. Triphenylchloromethane, for example, reacts readily with silver nitrate, whilst the acetochlorides of iron prepared by Scheurer-Kestner, are

but slowly acted on by the same reagent. Again, a freshly prepared solution of the double sulphate, obtained by heating chrome alum at 110°, gives no precipitate with barium chloride. In the case of the ethers, the double decomposition resulting in the removal of their electronegative elements or radicles is preceded by the hydrolysis of the ethers, and the author considers it possible that, in the case of slowly reacting salts, such as those above instanced, a similar hydrating action is a necessary preliminary. A. C. C.

Hydrocyanorosaniline. By AUGUSTE ROSENSTIEHL (*Bull. Soc. Chim.*, 1896, [iii], **15**, 959—964).—The author combats the views expressed by Tortelli on the constitution of rosanilines, views based chiefly on the properties of Hugo Müller's rosaniline hydrocyanide and that which Tortelli obtained from the double cyanide of pararosaniline and mercury (Abstr., 1895, i, 540). He gives reasons for maintaining that his pararosaniline formula is more in accordance with known reactions than those proposed by Fischer and by Nietzki. A. C. C.

Derivatives of Benzophenone. By PIETRO BARTOLOTTI (*Gazzetta*, 1897, **27**, i, 280—288).—The author describes a more rapid process than the one he has previously given (this vol., i, 193) for preparing benzoguaiacol directly from guaiacol.

Acetylbenzoguaiacol, $COPh \cdot C_6H_3(OMe) \cdot OAc$, is prepared by heating benzoguaiacol with acetic anhydride and dry sodium acetate on an oil bath; it crystallises in colourless prisms melting at 105—106°, and is insoluble in soda.

Benzoylveratrol (methylbenzoguaiacol), $COPh \cdot C_6H_3(OMe)_2$ [$(OMe)_2$ = 1:2], may be prepared by heating benzoguaiacol with methylic iodide and potash, or by heating veratrol with benzoic chloride and zinc chloride; it separates from alcohol in white crystals which melt at 101—102°.

Dinitrobenzoguaiacol, $COPh \cdot C_6H(NO_2)_2(OMe) \cdot OH$, is prepared by gradually adding an acetic acid solution of benzoguaiacol to fuming nitric acid; it separates from alcohol in thin, yellow crystals melting at 188—189°, and dissolves in hot soda, but separates as an oil on cooling.

1 : 2-*Dihydroxybenzophenone*, $COPh \cdot C_6H_3(OH)_2$, separates from the hydriodic acid mother liquors obtained during the determination of methoxyl in benzoguaiacol, acetylbenzoguaiacol and benzoylveratrol by Zeisel's method; it crystallises from water in long, white prisms containing $1H_2O$, which is lost at 110°; it then melts at 134°. It is probably identical with Döbner's benzoylpyrocatechol (Abstr., 1882, 507), although the latter is said to melt at 145°; both give a dibenzoyl-derivative melting at 95°, and a green colour with ferric chloride, changing to red on the addition of ammonium carbonate. W. J. P.

Parabenzoyltoluene Derivatives. By PAUL BOURCET (*Bull. Soc. Chim.*, 1896, [iii], **15**, 945—952).—For the preparation of the necessary parabenzoyltoluene, the author finds the method of Friedel and Crafts by far the most satisfactory. By employing a large excess of toluene (1000 grams of toluene, 50 grams of aluminium chloride, and 100 grams of benzoic chloride), and by adding the benzoic

chloride little by little to the mixture of toluene and aluminium chloride, the formation of greenish, viscous bye-products, which are very difficult to remove, is avoided, and 92 per cent. of the theoretical yield can be obtained.

Parabenzoylbenzylic bromide, $C_6H_4Bz\cdot CH_2Br$, is obtained by heating a mixture of parabenzoyltoluene with bromine in molecular proportion at 150°. The viscous mass is thoroughly washed with cold water and dissolved in alcohol, ether, chloroform, light petroleum, or toluene, from any of which solvents it separates in colourless, monoclinic crystals, which are weakly birefractive, and melt at 96·6°. On oxidation with an alkaline solution of potassium permanganate, parabenzoylbenzoic acid, melting at 194—195°, is obtained. *Parabenzoylbenzylic alcohol*, $C_6H_4Bz\cdot CH_2\cdot OH$, is obtained by boiling 25 grams of the above bromide for 6 hours with 2 litres of a 2 per cent. solution of potassium carbonate. After several crystallisations from boiling water, it forms nacreous, feathery plates (monoclinic) melting at 48·3°. It is very slightly soluble in cold, but fairly soluble in hot water, and is very soluble in alcohol, ether, chloroform, and acetone. The *acetate*, $C_6H_4Bz\cdot CH_2\cdot OAc$, is prepared by boiling parabenzoylbenzylic bromide with a large excess of a 3 per cent. solution of potassium acetate for 6 hours. After filtering off the unattacked bromide, the filtrate is evaporated to dryness and extracted with ether, from which the acetate separates in slender needles melting at 36°. It is very soluble in hot water, slightly less in cold, and very soluble in alcohol, ether, acetone, and chloroform.

Parabenzoyldiphenylmethane, $C_6H_4Bz\cdot CH_2\cdot C_6H_5$, prepared by acting on parabenzoylbenzylic bromide (25 grams) with benzene (250 grams) in the presence of aluminium chloride (15 grams), is a colourless substance, crystallising in the rhombic system, and melting at 157°. It is very soluble in benzene, chloroform, or boiling acetic acid, only slightly so in cold water, alcohol, ether, and acetone, and almost insoluble in light petroleum.

Parabenzoylbenzylidenic dibromide, $C_6H_4Bz\cdot CHBr_2$, is prepared by allowing bromine (35 grams) to fall drop by drop into parabenzoyltoluene (24 grams) heated to 170°; the solid product crystallises from boiling alcohol in small, colourless, monoclinic crystals melting at 86·8° and soluble in ether, chloroform, and benzene. On oxidation with an alkaline solution of potassium permanganate, it yields parabenzoylbenzoic acid. *Parabenzoylbenzaldehyde*, $C_6H_4Bz\cdot COH$, is obtained from the preceding compound by heating it with water in sealed tubes for 10 hours at 180°, calcium carbonate being used to neutralise the hydrobromic acid formed. The liquid in the tubes, after filtration from the excess of calcium carbonate and from the unattacked bromide, deposits crystals as it cools, which, on recrystallisation from boiling water, separate in nacreous plates melting at 64·2°. It forms a crystalline compound with sodium hydrogen sulphite, and is very soluble in water, alcohol, ether, or chloroform, but insoluble in light petroleum, benzene, and toluene.

Parabenzoyltriphenylmethane, $C_6H_4Bz\cdot CHPh_2$.—Aluminium chloride (30 grams) is added gradually to a boiling solution of parabenzoylbenzylidenic dibromide (50 grams) in benzene (500 grams). After

evaporating the excess of benzene, small, reddish crystals are obtained which are purified by repeated crystallisation from benzene or from boiling acetic acid. This substance forms small, rhombic crystals which are at first colourless, but become slightly red on exposure to the air; it melts at 164°. It is soluble in hot acetic acid, chloroform, or benzene, and slightly so in ether, alcohol, and light petroleum. *Parabenzoyltriphenylcarbinol*, $C_6H_4Bz\cdot CPh_2\cdot OH$, is obtained by oxidising the preceding compound, dissolved in glacial acetic acid, with an acetic acid solution of chromic acid, the latter being added little by little until the red colour remains permanent. On diluting with water, a white substance separates which can be purified by first dissolving it in glacial acetic acid, precipitating with water, and then crystallising it from boiling acetic acid. It forms large, colourless, monoclinic crystals melting at 158°, and is very soluble in chloroform, benzene, and glacial acetic acid, but only slightly so in alcohol, ether, or light petroleum.

A. C. C.

Isoxazolones [Phenylisoxazolones]. By PAUL RABE (*Ber.*, 1897, **30**, 1614—1617. Compare Schiff, this vol., i, 444, 493, and Claisen, *ibid.*, 493).—Phenylisoxazolone, melting at 152°, reacts with benzoic chloride and sodium hydroxide solution, or, in benzene solution, with benzoic chloride and pyridine, yielding a mixture of two isomeric *benzoyl* derivatives. The α-derivative is formed in largest quantity by the Schotten-Baumann method, and it can be separated from the isomeric β-compound by recrystallisation from absolute alcohol, in which it is less soluble; it crystallises in colourless needles melting at 161°, and is readily soluble in ether and benzene, but insoluble in water, alkalis, or acids. Alcoholic potash readily hydrolyses it, as does also an acetic acid solution of phenylhydrazine, the latter yielding symmetrical benzoylphenylhydrazine and phenylisoxazolone. The *β-compound* is formed almost exclusively by the second method given above; it crystallises in colourless prismatic needles melting at 115°, and is insoluble in water, but dissolves in the usual organic solvents more readily than the α-compound. In chemical properties, it resembles its isomeride. The provisional formulæ given for the two compounds are $\begin{matrix}CH\text{—}CO\\ \Vert \\ CPh\cdot NBz\end{matrix}\!\!>\!O$ and $\begin{matrix}CH\!:\!C(OBz)\\ | \\ CPh\text{===}N\end{matrix}\!\!>\!O$.

J. J. S.

Condensation Products of Chloral with Alkyl Derivatives of Metahydroxybenzoates and Symmetrical Dihydroxybenzoates: Synthesis of Alkylated Monhydroxy- and Dihydroxy-phthalic Acids. By PAUL FRITSCH (*Annalen*, 1897, **296**, 344—361).—*Ethylic metamethoxybenzoate* boils at 163° under a pressure of 50 mm., and the *ethoxy*-derivative boils at 172—173° under a pressure of 50 mm.; *ethylic* 1 : 3 : 5-*dimethoxybenzoate* and *ethylic* 1 : 3 : 5-*diethoxybenzoate* melt at 26—27° and 19—20° respectively, and boil at 199—200° and 212° under a pressure of 50 mm.

When these salts are agitated with chloral hydrate and concentrated sulphuric acid, the corresponding substitution products of trichloromethylphthalide are formed, having a constitution represented by the general formula, $C_6H_{4-x}(OR)_x\!<\!\begin{matrix}CO\\ CH(CCl_3)\end{matrix}\!>\!O$. 5-*Methoxytrichloro-*

methylphthalide and 5-*ethoxytrichloromethylphthalide* melt at 135° and 118° respectively; 3 : 5-*dimethoxytrichloromethylphthalide* and 3 : 5-*diethoxytrichloromethylphthalide* melt at 125° and 113° respectively.

Treatment of the substituted trichloromethylphthalides with hot aqueous alkalis converts them into the phthalidecarboxylic acids, $C_6H_{4-x}(OR)_x{<}{\overset{CO}{\underset{CH(COOH)}{}}}{>}O$. 5-*Methoxyphthalidecarboxylic acid* 5-*ethoxyphthalidecarboxylic acid*, 3 : 5-*dimethoxyphthalidecarboxylic acid*, and 3 : 5-*diethoxyphthalidecarboxylic acid* melt at 169—170°, 128°, 183°, and 172—173° respectively; the *methylic* salts melt at 95°, 79—80°, 142—143°, and 108° respectively.

Elimination of carbonic anhydride from the foregoing acids gives rise to the corresponding substituted phthalides, $C_6H_{4-x}(OR)_x{<}{\overset{CO}{\underset{CH_2}{}}}{>}O$. 5-*Methoxyphthalide*, 5-*ethoxyphthalide*, 3 : 5-*dimethoxyphthalide*, and 3 : 5-*diethoxyphthalide* melt at 120°, 87°, 166—167°, and 179° respectively.

Oxidation of the phthalides with potassium permanganate in alkaline solution converts them into the phthalic acids. 5-Methoxyphthalic acid and anhydride melt at 164° and 97°, and not, as stated by Schall, at 138—144° and 93° respectively. 3 : 5-*Dimethoxyphthalic acid* and 3 : 5-*diethoxyphthalic acid* melt at 158° and 182° respectively, and the *anhydrides* at 147° and 130°. Fusion of these acids with metadialkylamidophenols gives rise to rhodamines which dye animal fibre; sparingly soluble monosulphonic acids, which also behave as colouring matters, are obtained from these rhodamines by the action of fuming sulphuric acid.

If the oxidation of 5-methoxyphthalidecarboxylic acid is carried out with a solution of potassium permanganate at 60°, and the product neutralised with barium carbonate, the *barium* salt of 5-methoxyphthalonic acid, $COOH{\cdot}C_6H_3(OMe){\cdot}CO{\cdot}COOH$, is obtained in transparent needles containing $2H_2O$. The phenylhydrazine *compound*, $C_{16}H_{12}N_2O_4$, crystallises in small needles, and melts at 223°; the metadimethylamidophenol *compound*, $C_{18}H_{17}NO_6$, becomes violet on exposure to the atmosphere, and melts at 180°. M. O. F.

Action of Potassium Hydroxide on Orthomethoxysulphaminebenzoic Acid. By CHARLES WALKER (*Amer. Chem. J.*, 1897, **19**, 578—580).—When *orthomethoxysulphaminebenzoic acid*

$$OMe{\cdot}C_6H_3(SO_2{\cdot}NH_2){\cdot}COOH$$

(compare Bromwell, this vol., i, 564) is fused with potassium hydroxide at a dull red heat for 5 to 8 minutes, the product is *orthohydroxysulphaminebenzoic acid*, $OH{\cdot}C_6H_3(SO_2{\cdot}NH_2){\cdot}COOH$; the stability of the sulphonamide group is remarkable. The new acid melts and decomposes at 231°; the *sodium* salt, with $1\frac{1}{2}H_2O$; *calcium*, with $6H_2O$; *barium*, with $4H_2O$, and *silver* salts were prepared and analysed.

When orthomethoxysulphaminebenzoic acid is heated with strong hydrochloric acid at 150—160° for 3 hours in a sealed tube, the product is salicylic acid. C. F. B.

Metadihydroxy-β-phenylcoumarin. By GIUSEPPE BRUNI (*Gazzetta*, 1897, **27**, i, 574—576).—Ciamician and Silber have described metamethoxyhydroxy-β-phenylcoumarin and its acetyl derivative as being

yellow (Abstr., 1894, i, 255), although dihydroxyphenylcoumarin and its diacetate are both white; the author finds that the difference in colour is due to slight impurity, and not to difference of constitution. The two former substances are both white. W. J. P.

Action of Tannin on some Alkaloids. By WILLIAM OECHSNER DE CONINCK (*Compt. rend.*, 1897, **124**, 506—508).—When dry tannin is added to pyridine, it dissolves slowly without producing any precipitate, and the liquid, when left over sulphuric acid, dries up to a viscous, plastic mass insoluble in water; when tannin is added to a concentrated aqueous solution of pyridine, it behaves in a similar manner. Similar results are obtained when dry tannin is added to piperidine or nicotine, either pure or in concentrated aqueous solution.

When, however, concentrated aqueous solutions of tannin and of pyridine containing these substances in molecular proportion are mixed, a white precipitate is formed, consisting of a compound of 1 mol. of pyridine with 1 mol. of tannin. With piperidine, a similar result is obtained, but the white precipitate rapidly darkens. Experiments are recorded showing the extent to which solutions of pyridine and piperidine must be diluted in order to prevent their precipitation by tannin.
A. C. C.

Action of Tannin and of other Aromatic Derivatives on some Alkaloids and Compound Ureas. By WILLIAM OECHSNER DE CONINCK (*Compt. rend.*, 1897, **124**, 562—563).—Neither dry tannin nor an alcoholic solution of tannin gives any precipitate when added to a solution of pyridine in an equal volume of absolute alcohol, but on the addition of water a precipitate at once forms. With an alcoholic solution of piperidine, an emerald-green coloration is produced on the addition of dry tannin, and an immediate white precipitate on the addition of an alcoholic solution of tannin. Neither dry tannin nor an ethereal solution of tannin gives any precipitate when added to an ethereal solution of pyridine; a white precipitate is, however, formed on the addition of water. With an ethereal solution of piperidine, a solution of tannin in ether gives a precipitate, but dry tannin does not. The following reactions serve to readily distinguish between pyridine and piperidine.

A freshly prepared solution of gallic acid produces neither precipitate nor coloration when added to an aqueous solution of pyridine; with piperidine, a pale rose coloration is at first produced, becoming darker in colour, and finally of a deep yellow. With pyridine, pyrogallol gives a pale yellow coloration appearing only after some time, but with piperidine an immediate yellow coloration, becoming in turn deep yellow, dark brown, and brownish-black. Catechol gives no reaction with pyridine, but with piperidine a violet coloration at first, becoming successively pink and yellow.

Quinol gives no reaction with pyridine, but with piperidine a yellow colour turning to a deep brown. Resorcinol, phloroglucinol, and orcinol give no reactions either with pyridine or piperidine in aqueous solution.

Tannin gives neither coloration nor precipitate when added to benzylcarbamide, diphenylcarbamide, phenylcarbamide, methylcarbamide, or diphenylthiourea in either aqueous, alcoholic, or ethereal solutions.
A. C. C.

Preparation of Ethylic Phenylacetate. By WILHELM WISLICENUS (*Annalen*, 1897, **296**, 361—362).—Difficulty having sometimes arisen in preparing ethylic phenylacetate from benzylic cyanide, the author describes in detail the method which he adopts. M. O. F.

Oximes of Mucophenoxychloric and Mucophenoxybromic Acids; the Action of Aluminium Chloride and Benzene on Mucochloric and Mucobromic Acids. By HENRY BARKER HILL, JOHN A. WIDTSOE, and FREDERICK L. DUNLAP (*Amer. Chem. J.*, 1897, **19**, 627—649).—By HENRY B. HILL (introduction).—Whereas methylic mucobromate, unlike the free acid, does not react with hydroxylamine to form an oxime (Hill and Cornelison, Abstr., 1894, i, 322), it is now found that methylic mucophenoxybromate, on the other hand, reacts no less readily than the corresponding acid. Mucochloric chloride reacts with benzene in the presence of aluminium chloride, forming a dichlorodiphenylcrotonic acid which yields diphenylacetic acid when oxidised; this can be explained by assuming the hydroxylactone constitution for mucochloric acid, when its chloride would be represented by the first of the following formulæ:

$$\left.\begin{array}{l} CCl\cdot CHCl \\ \| \\ CCl\cdot CO \end{array}\right> O \qquad\qquad \begin{array}{l} CCl\cdot CHO \\ \| \\ CCl\cdot COCl \end{array}$$

Lactone-formula. Aldehyde-formula.

had the acid the aldehyde constitution, its chloride would have the second of the formulæ given, and should form an aldehyde-phenyl-ketone with benzene and aluminium chloride.

By JOHN A. WIDTSOE (p. 631).—*Methylic mucophenoxybromate*, $OPh\cdot C_4HBrO_3Me$, made by mixing the silver salt of the acid with methylic iodide, melts at 75—76°; it reacts with hydroxylamine hydrochloride, yielding a product, $OPh\cdot C_4H_2BrNO_3Me$, which can also be obtained by boiling the *silver* salt of mucophenoxybromoxime with methylic iodide. This product melts at 150—165° (at 168—170° when heated rapidly); it cannot be obtained by boiling the oxime with the alcohol and a little hydrochloric acid, but the corresponding *ethylic* derivative, which crystallises in flat, silky needles and melts at 122—124°, can be obtained in this way. When gaseous hydrogen chloride is passed into an alcoholic solution of mucophenoxybromoxime, the temperature not being allowed to rise above 20°, *mucophenoxybromoxime anhydride*, $OPh\cdot C_4HBrNO_2$, separates. This melts at 121° (at 124—126° when heated rapidly). When its alcoholic solution is boiled, with or without the addition of hydrochloric acid, it undergoes a molecular transformation into *phenoxybromomaleimide*; this melts at 144—145°, or at 148—150° when heated rapidly; it will crystallise with 1 mol. of methylic alcohol, forms a silver salt, and is converted by alkalis into phenoxybromomaleic acid, as is also the oxime anhydride.

A series of analogous chlorine compounds was prepared by the same methods. *Methylic mucophenoxychlorate* melts at 59°; its oxime, identical with the methylic derivative of mucophenoxychloroxime, melts at 156—160°, or at 162—166° when heated rapidly. *Mucophenoxychloroxime anhydride* (precipitated by the addition of water to the

alcoholic hydrochloric acid solution) melts at 96—98°. *Phenoxychloromaleimide* melts at 118—119°; it will crystallise with 1 mol. of methylic alcohol.

By FREDERICK L. DUNLAP (p. 641).—The action of benzene and aluminium chloride on mucochloric and mucobromic acids (which are more suitable than their respective chlorides and bromides) was studied by dissolving the acid in 5 times its weight of benzene diluted with twice its volume of carbon bisulphide, adding $1\frac{1}{2}$ times its weight of aluminium chloride, heating in a reflux apparatus until the evolution of hydrogen chloride ceased, distilling off the solvent, washing the solidified residue with benzene, and recrystallising it from acetic acid. *Mucochloric chloride* boils at 100—101° under 15 mm. pressure. *Dichlorodiphenylcrotonic acid,* $C_4H_2Ph_2Cl_2O_2$, melts at 152°; the *barium* and *calcium* salts both crystallise with $2H_2O$; the acid is oxidised by alkaline permanganate to diphenylacetic acid, and reduced by sodium amalgam to *γ-diphenylbutyric* acid, which melts at 106°, and forms amorphous *silver, calcium,* and *barium* salts, the first of which was analysed.

Dibromodiphenylcrotonic acid melts at 146—147°; the *barium* salt, with $3H_2O$; *calcium* salt, with $2H_2O$, and the amorphous *silver* salt were prepared and analysed; the *methylic* salt obtained by heating the acid with methylic alcohol and sulphuric acid melts at 79—80°. When reduced, it yields the same products as dichlorodiphenylcrotonic acid, and when it is boiled with aqueous sodium carbonate in a reflux apparatus, the product formed is probably *diphenylbromallylene,* for it unites with bromine without evolution of hydrogen bromide, yielding a *dibromide,* $C_{15}H_{11}Br_3$, which melts between 120 and 130°. C. F. B.

Hydroxytrimethylindoline (Trimethylindolinone). By ANTONIO PICCININI (*Gazzetta,* 1897, **27**, i, 473—480).—By the condensation of isobutaldehyde with phenylmethylhydrazine, Brunner (Abstr., 1896, i, 625) obtained a base of the composition $C_{11}H_{15}NO$, which yielded a trimethylindolinone on oxidation with silver nitrite; the same indolinone was prepared by Ciamician and Piccinini (this vol., i, 101) by oxidising Ferratini's (Abstr., 1893, i, 603) and Fischer's trimethyldihydroquinoline. Further, Ciamician and Piccinini (*loc. cit.*) obtained Brunner's base by reducing the indolinone with sodium and alcohol.

The author considers Brunner's base to be 2′-*hydroxy*-1′ : 3′ : 3′-trimethylindoline, $C_6H_4{<}^{CMe_2}_{NMe}{>}CH{\cdot}OH$ (compare Brunner, *loc. cit.*); it melts at 97—98°, and readily combines with methylic iodide, yielding a *methiodide,* $OH{\cdot}C_{10}H_{11}NMe,MeI$, which crystallises in colourless prisms melting and decomposing at 165°. This is converted by moist silver oxide into a substituted ammonium *hydroxide,* which has a strongly alkaline reaction.

On heating the methiodide with potash, 2′-*methoxy*-1′ : 3′ : 3′-*trimethylindoline,* $C_6H_4{<}^{CMe_2}_{NMe}{>}CH{\cdot}OMe$, distils and is ultimately obtained in colourless prisms which melt at 41° and sublime at the ordinary temperature; its *picrate* blackens at 150° and melts at 230°, and its *platinochloride,* $(C_{12}H_{17}NO)_2,H_2PtCl_6$, crystallises in yellow

laminæ melting and undergoing decomposition at 209—210°. On heating the base with hydrogen iodide and red phosphorus at 150°, distilling the product in a current of steam, concentrating, and crystallising the residual liquor, the hydriodide of the tertiary base, $C_{10}H_{12}NMe$, is obtained (compare Ciamician and Piccinini, *loc. cit.*). The *methiodide*, $C_{12}H_{17}NO,MeI$, obtained by direct combination, crystallises in colourless, lustrous prisms melting at 183—184°; it gives a substituted ammonium *hydroxide* of strongly alkaline reaction when treated with moist silver hydroxide. W. J. P.

Researches on Organic Additive Products.—Triphenylmethane and Benzene. By BASIL B. KURILOFF (*Zeit. physikal. Chem.*, 1897, **23**, 547—557).—Triphenylmethane and benzene form an additive product of the composition $CH(C_6H_6)_3,C_6H_6$, which is stated to melt at 76°. Linebarger investigated solutions of triphenylmethane in benzene, and considered that the compound was decomposed into its components above 37·5°. The author, therefore, reinvestigated the solubility relations, and obtained perfectly regular results, the curve exhibiting three portions for the equilibrium of (1) solid benzene and solution, (2) compound and solution, (3) triphenylmethane and solution. The two latter curves cut at about 74°, and at 78·2° the composition of the solution corresponds with that of the compound, and below this temperature may contain more or less benzene, that is, the curve here gives the lowering of the melting point (78·2) of the compound by the addition either of benzene or of triphenylmethane. Cryoscopic and boiling point observations gave a normal molecular weight for triphenylmethane when the formation of the compound is allowed for, so that the behaviour throughout is perfectly normal and in accord with the existence of the additive compound. L. M. J.

Action of Nitric Acid on Triphenylmethane. By E. S. SMITH (*Amer. Chem. J.*, 1897, **19**, 702—703).—On one occasion, when nitric acid of sp. gr. 1·34 and then fuming nitric acid were added in indefinite quantities to triphenylmethane, the mixture allowed to remain for a short time, heated on the sand-bath for a few minutes, and then poured into water, the product consisted largely of triphenylcarbinol. Attempts to repeat the experiment have been unsuccessful.

C. F. B.

Addition of Halogen to Halogenised and Phenyl Derivatives of Ethylene. By HEINRICH BILTZ (*Annalen*, 1897, **296**, 263—278. Compare this vol., i, 533).—The indifference of tetraphenylethylene towards bromine is attributed by the author to the arrangement of the substituent radicles in space. Other unsaturated compounds have been therefore investigated from this point of view.

Diphenyldichlorodibromethane, $CPh_2Br\cdot CCl_2Br$, obtained from diphenyldichlorethylene and bromine, crystallises from alcohol in lustrous, refractive leaflets, melts at 120—120·5°, and may be distilled without undergoing decomposition; it develops a magenta-red coloration with a solution of potassium dichromate in concentrated sulphuric acid.

Diphenyltetrachlorethane, $CPh_2Cl\cdot CCl_3$, prepared from diphenyldichlorethylene and chlorine, crystallises from alcohol in prismatic

needles melting at 85°. Alcoholic potash eliminates chlorine, and gives rise to diphenyldichlorethylene.

Phenyltrichlorethane, $CHPhCl{\cdot}CHCl_2$, is obtained by saturating with chlorine a solution of ω-chlorocinnamene in chloroform; it boils at 134° under a pressure of 19 mm., and at 254·5—255·5° under atmospheric pressure, a part undergoing decomposition. The sp. gr. = 1·3622 at 15°/4°, and the refractive index $n_D = 1{\cdot}5652$, whence the molecular refraction $M = 50{\cdot}03$.

Phenyldichlorethylene, $CHPh{:}CCl_2$, prepared from phenyltrichlorethane and alcoholic potash, boils at 103·5°, 123°, and 225° under pressures of 15 mm., 32 mm., and 774 mm. respectively; it has a sp. gr. = 1·2651 at 15°/4°, the refractive index $n_D = 1{\cdot}5899$, and the molecular refraction $M = 46{\cdot}09$.

Phenyltetrachlorethane, $CHPhCl{\cdot}CCl_3$, is formed from the foregoing substance when chlorine is passed into the solution in chloroform; it is colourless and odourless, and boils at 138—139°, 148°, and 267—268° under pressures of 12 mm., 21 mm., and 773 mm. respectively. The substance has a sp. gr. = 1·453 at 15°/4°, and the refractive index $n_D = 1{\cdot}5718$, whence the molecular refraction $M = 55{\cdot}16$.

Phenyltrichlorethylene, $CClPh{:}CCl_2$, is prepared by the action of alcoholic potash on phenyltetrachlorethane, and boils at 121°, 130°, and 235° under pressures of 23 mm., 31 mm., and 751 mm. respectively; the sp. gr. = 1·376 at 15°/4°, the refractive index $n_D = 1{\cdot}5861$, and the molecular refraction $M = 50{\cdot}54$.

Phenylpentachlorethane, $CCl_2Ph{\cdot}CCl_3$, is obtained by passing chlorine into a solution of the foregoing compound in chloroform. It separates from alcohol or glacial acetic acid in lustrous, rhombic crystals, melts at 37—38°, and boils at 178—179° under a pressure of 34 mm. *Nitrophenylpentachlorethane*, $NO_2{\cdot}C_6H_4{\cdot}CCl_2{\cdot}CCl_3$, is produced by the action of fuming nitric acid; it separates from alcohol in colourless, monoclinic crystals, and melts at 114°.

Phenyl-ω-chloro-aω-dibromethane, $CHPhBr{\cdot}CHClBr$, is prepared from ω-chlorocinnamene by the action of bromine, and boils at 165° under a pressure of 26 mm.; it crystallises from dilute alcohol in colourless, triclinic needles, and melts at 32°.

Phenyl-ωω-dichloro-aω-dibromethane, $CHPhBr{\cdot}CCl_2Br$, is obtained from phenyldichlorethylene and undiluted bromine; it is a viscous, yellowish oil, and distils at 175° under a pressure of 24 mm., evolving bromine.

Phenyl-aωω-trichloro-aω-dibromethane, $CPhClBr{\cdot}CCl_2Br$, produced by the action of undiluted bromine on phenyltrichlorethylene, separates from alcohol in rhombic crystals melting at 47—48°.

Phenyldichlorethane, $CHPhCl{\cdot}CH_2Cl$, has not been previously obtained in the purified state. It boils at 114·5—115·5° under a pressure of 15 mm., and scarcely undergoes change when distilled under the ordinary pressure at 233—234°; its sp. gr. = 1·240 at 15°/4°, and the refractive index $n_D = 1{\cdot}554$, whence the molecular refraction $M = 45{\cdot}21$.

Consideration of the foregoing compounds shows that, in the case of phenylethane derivatives, the atomic refraction of chlorine increases with the number of halogen atoms; in the phenylethylene series,

however, this constant decreases as substitution becomes more complete. M. O. F.

Action of Carbamide on Quinones. By Siro Grimaldi (*Gazzetta*, 1897, **27**, i, 228—246. Compare Abstr., 1895, i, 425).—After boiling phenanthraquinone with carbamide in acetic acid solution in a reflux apparatus for 24 hours, and cooling the solution, a *monoureine*, $C_6H_4<\begin{matrix}C_6H_4\\ -CO-\end{matrix}>C<\begin{matrix}NH\\ NH\end{matrix}>CO$, separates; it crystallises in white needles melting at 299°, and its solution in dilute acetic acid is fluorescent. On boiling with hydroxylamine acetate in acetic acid solution, it gives a crystalline *oxime*, $CO<\begin{matrix}NH\\ NH\end{matrix}>C<\begin{matrix}C(N\cdot OH)\\ -C_6H_4-\end{matrix}>C_6H_4$; this melts at 200—202°, and is hydrolysed by boiling with dilute hydrochloric acid. A *dinitro*-derivative, $C_6H_4<\begin{matrix}C_6H_4\\ -CO-\end{matrix}>C<\begin{matrix}N(NO_2)\\ N(NO_2)\end{matrix}>CO$, is obtained on heating the ureine with nitric acid in sealed tubes; it crystallises in yellow needles which deflagrate on heating.

The *diureine*, $\begin{matrix}CO\cdot NH & \diagup C_6H_4\cdot C_6H_4 \diagdown & NH\cdot CO\\ NH\cdot C & \overline{\qquad\qquad\qquad} & C-NH\end{matrix}$, prepared by heating phenanthraquinone with carbamide in an oil bath at 250°, is an amorphous, white powder which decomposes on heating. When treated with a mixture of sulphuric and fuming nitric acids, it yields a *dinitro*-derivative, $C_{16}H_{10}N_6O_6$; this crystallises in yellow needles which deflagrate at 300°, and by analogy with diacetyldiphenylacetylenediureine (Angeli, Abstr., 1890, 1290) and dinitrodimethylacetylenediureine (Franchimont and Klobbie, Abstr., 1889, 125) must contain the group $>C<\begin{matrix}N(NO_2)\\ N(NO_2)\end{matrix}>CO$.

β-Naphthaquinonemonoureine, $O:C_{10}H_6<\begin{matrix}NH\\ NH\end{matrix}>CO$, is prepared by boiling β-naphthaquinone with carbamide in acetic acid solution; it melts at 162—163°, and yields a crystalline *oxime*, $C_{11}H_9N_3O_2$, and a *dinitro*-derivative, $O:C_{10}H_6<\begin{matrix}N(NO_2)\\ N(NO_2)\end{matrix}>CO$; the latter crystallises in yellow needles which deflagrate when strongly heated. A white *diureine*, $CO<\begin{matrix}NH\\ NH\end{matrix}>C_{10}H_6<\begin{matrix}NH\\ NH\end{matrix}>CO$, is obtained by heating a mixture of β-naphthaquinone and carbamide at 200° in an oil bath; it yields a *dinitro*-compound, $CO<\begin{matrix}NH\\ NH\end{matrix}>C_{10}H_6<\begin{matrix}N(NO_2)\\ N(NO_2)\end{matrix}>CO$, crystallising in yellow needles which deflagrate on heating.

Quinonemonoureine, $CO<\begin{matrix}CH:CH\\ CH:CH\end{matrix}>C<\begin{matrix}NH\\ NH\end{matrix}>CO$, is formed on boiling quinone with carbamide in acetic acid solution, but is best prepared by heating quinone with carbamide for 8—10 hours at 140—150° in a sealed tube; it crystallises in yellow needles which do not melt at 320°, and yields a crystalline oxime,

$$CO<\begin{matrix}NH\\ NH\end{matrix}>C<\begin{matrix}CH:CH\\ CH:CH\end{matrix}>C:N\cdot OH,$$

and a *dinitro*-derivative, $C_7H_4N_4O_6$.

Anthraquinonemonoureine, $CO{<}{\substack{C_6H_4\\C_6H_4}}{>}C{<}{\substack{NH\\NH}}{>}CO$, prepared by heating a mixture of anthraquinone and carbamide at 300°, is an amorphous substance which melts at above 320° with decomposition; it yields a crystalline *oxime*, $C_{15}H_{11}N_3O_2$, and a *dinitro*-derivative, $C_{15}H_8N_4O_6$, which crystallises in yellow needles. The author was unable to prepare the corresponding diureine.

Phenanthraquinone dithiodiureine, $\begin{array}{l}CS\cdot NH\\ \;\vert\qquad\;\vert\\ NH\cdot C\end{array}\!\!{<}{\substack{C_6H_4\cdot C_6H_4\\ \rule{3em}{0.4pt}}}{>}\!\!\begin{array}{l}NH\cdot CS\\ \;\vert\qquad\;\vert\\ C\text{—}NH\end{array}$, is obtained by heating a mixture of phenanthraquinone and thiocarbamide on an oil bath at 210°, and is purified by precipitating its sulphuric acid solution with water; it forms a crystalline, red powder which melts and decomposes at above 320°. W. J. P.

Nitro-compounds of Anthragallol. By Max Bamberger and Fritz Böck (*Monatsh.*, 1897, **18**, 283—301).—Dry anthragallol, purified by removing the admixed benzoic acid by sublimation and recrystallising the residue from alcohol, is added in small portions at a time to fuming nitric acid, taking care that the temperature never rises above −15°. As the reaction proceeds, *ψ-nitroanthragallol* separates in fine, dark-red crystals; these are collected as rapidly as possible, purified by washing with cooled water to which a little hydrochloric acid has been added, and dried in a vacuum over sulphuric acid. In the dry condition, it is quite stable, and dissolves without change in alcohol, ethylic acetate, chloroform, benzene, and xylene, forming a yellow to red solution, and in alkalis with a green colour. The same nitro-derivative is obtained when anthragallol is exposed to the fumes of nitric acid.

α-Nitroanthragallol is prepared by boiling the ψ-nitro-compound with water, when the violet colour of the solution disappears, and a yellowish-brown substance separates, which is purified by recrystallisation, first from alcohol, and then from a mixture of alcohol and light petroleum. During the reaction, gas is given off consisting of a mixture of carbonic anhydride, nitric oxide, and nitrogen. α-Nitroanthragallol, which crystallises from alcohol in beautiful, golden-brown, feathery needles, melts at 224°, is easily soluble in ether, benzene, and chloroform, but insoluble in water and light petroleum. It dissolves in alkalis with a green, and in concentrated sulphuric acid with a red to brown, coloration. On oxidation with dilute nitric acid, phthalic acid is produced, thus showing that the nitro-group is contained in the same ring as the three hydroxyl groups.

When α-nitroanthragallcl is covered with ammonia solution, and hydrogen sulphide is passed through the liquid, the green solution changes to brown and *amido-anthragallol* separates; this crystallises from ethylic acetate in groups of prismatic needles, is soluble in water, alcohol, ethylic acetate, and benzene, forming a red solution, and in alkalis with a dark bluish-red colour. If an acid is added to the solution, it becomes bright red, and a reddish-brown precipitate is formed.

β-Nitroanthragallol.—When ψ-nitroanthragallol is boiled with a small quantity of absolute alcohol, it dissolves with evolution of gas, and, on cooling, golden-yellow needles separate, which can be recrystallised from alcohol; the gas consists of a mixture of ethylic

nitrite, carbonic anhydride, oxygen, and nitrogen. On oxidation, phthalic acid is obtained, showing that, in this compound also, the nitro-group must be attached to the same ring as the hydroxyl groups. An amido-anthragallol, which crystallises from ethylic acetate in small needles having a feeble greenish-metallic lustre, can be prepared from β-nitro-anthragallol by the method described above.

Tribenzoylanthragallol, obtained by the action of benzoic chloride on anthragallol, crystallises from ethylic acetate in small, yellow plates melting at 207°. By the action of fuming nitric acid, it is converted into a *nitrobenzoylanthragallol*, which crystallises from glacial acetic acid in beautiful golden-yellow plates melting at 209°.

The probable constitution of the various nitro-compounds is discussed and an account of their absorption spectra given. A. W. C.

Action of Sodium on Camphor. By GIUSEPPE ODDO (*Gazzetta*, 1897, **27**, i, 203—207).—Baubigny (*Ann. chim. phys.*, 1870, [iv], **19**, 121) only succeeded in preparing a monosodio-derivative of camphor, but Brühl (Abstr., 1892, 200) obtained evidence of the formation of disodiocamphor during the preparation of ethylcamphor. Since the author has previously shown (see following abstract) that the sodio-derivative of dicamphor is readily oxidised by atmospheric oxygen to dicamphanhexane-1:4-dione, if camphor yields a disodio-derivative, this should be oxidised by atmospheric oxygen to sodiodicamphor. The author finds that, on treating camphor with sodium in toluene solution, the product contains small quantities of the dicamphor derivatives which he has previously prepared from dicamphor; he therefore concludes that camphor, like benzophenone and some other ketones, does yield a disodio-derivative.

The author confirms Beckmann's observation (Abstr., 1894, i, 614) respecting the formation of camphopinacone ($\alpha\alpha$-dicamphandiol),

$$C_8H_{14}<\begin{matrix}CH_2-CH_2- \\ | \quad\quad | \\ C(OH)C(OH)\end{matrix}>C_8H_{14},$$

on treating camphor with sodium in ethereal solution. Unlike the $\beta\beta$-dicamphor compounds, this substance is not converted into camphor by prolonged boiling with sodium in toluene solution. W. J. P.

Action of Sodium on Dicamphor and Dicamphanhexane-1:4-dione. By GIUSEPPE ODDO (*Gazzetta*, 1897, **27**, i, 197—202).—Sodium acts on $\beta\beta$-dicamphor and on dicamphanhexane-1:4-dione in toluene solution, with formation of a mixture of these two substances with camphor, borneol, and the mixture of acids obtained by treating bromocamphor with sodium (this vol., i, 430). The dicamphanhexanedione is thereby converted into sodiodicamphor, $\begin{matrix}C_7H_{13}\cdot C & \text{——} & C & \text{——} & C_7H_{13} \\ | & | & | & | & | \\ CH & — & C(ONa)C(ONa)\cdot CH\end{matrix}$, and the dicamphor is converted into sodiocamphor, $\begin{matrix}C_7H_{13}\cdot CH \\ | \quad\quad\quad || \\ CH—C\cdot ONa\end{matrix}$; this, on hydrolysis, yields a labile modification of camphor of the constitution $\begin{matrix}C_7H_{13}\cdot CH \\ | \quad\quad\quad || \\ CH—C\cdot OH\end{matrix}$, which then changes into the stable form, $\begin{matrix}C_7H_{13}\cdot CH_2 \\ | \quad\quad\quad | \\ CH—CO\end{matrix}$.

The author considers that he has thus demonstrated the existence of the group $-CH_2\cdot CO\cdot CH\equiv$ in camphor, and therefore concludes that the constitutions which Kekulé and Bredt have assigned to camphor are erroneous. W. J. P.

Pinene; a Correction. By ALBERT REYCHLER. (*Bull. Soc. Chim.*, 1896, [iii], 15, 969—970).—The author modifies his view of the changes involved in the conversion of pinene into camphene (compare Abstr., 1896, i, 313 and 620). A. C. C.

Essence of Bitter Fennel. By E. TARDY (*J. Pharm.*, 1897, [vi], 6, 98—102).—The author has found the following substances in the essence of French-grown, bitter fennel, supplied by the Grasse Distillery; a bivalent, dextrogyrate terebenthene, phellandrene, cymene, fenchone, estragol, anethoil, anisaldehyde, anisic acetone,

$$MeO\cdot C_6H_4\cdot CH_2\cdot COMe,$$

identical with the substance previously obtained from essence of anise, anisic acid, and a crystalline compound, $C_{13}H_{14}O_2$, melting at 213°. J. J. S

Active Principles of some Aroideæ. By Mdlle. J. CHAULIAGUET, ALEXANDRE HÉBERT, and F. HEIM (*Compt. rend.*, 1897, **124**, 1368—1370).—Experiments were made with *Arum maculatum*, *A. italicum*, and *Arisarum vulgare*. The products obtained were (1) a glucoside having all the general properties of a saponin, and existing in all parts of the plant, but more especially in the root nodules, from which it seems to migrate in the spring to the subaërial parts of the plant. Its poisonous effects are similar to those of the sapotoxins, but are feebler, and it does not destroy the irritability of nerves and muscular striæ, and has scarcely any effect on the heart. (2) A very volatile, unstable, brown, liquid alkaloid, only slightly soluble in water, but soluble in all ordinary organic solvents. Both the base and its hydrochloride, which crystallises in very deliquescent needles, have a strong odour of mice. All its general properties are identical with those of conicine, but its poisonous properties are less active; it is probably an isomeride or a higher homologue. The existence in the *Aroideæ* of an alkaloid, or a close relation of an alkaloid, characteristic of such a very different natural order as the *Umbelliferæ*, is a point of considerable interest. A similar alkaloid also exists, together with saponin, in *Caladium bulbosum* and *Amorphophallus Rivieri*.

No evidence could be obtained of the existence of hydrocyanic acid either free or combined, in any of the *Aroideæ* examined.

C. H. B.

Spectra of Chlorophylls. By ALEXANDRE LÉON ÉTARD (*Compt. rend.*, 1897, **124**, 1351—1354).—When comparing the spectra of chlorophylls, it is essential to examine solutions of known concentration in a specified solvent and in layers of definite thickness, and the comparison is greatly facilitated by using the ordinary comparison prism. Chlorophyll extracted from perennial rye-grass (*Lolium perenne*) by carbon bisulphide and carefully freed from fats, alkaloids, free acids, &c., was examined in a carbon bisulphide solution containing one part in 10,000 and in a layer 150 mm. deep. It showed bands at λ 729—635; 635—598; 580—564;

559—549, and 528—507, the mean axes being approximately 682, 616·5, 572, 554, and 517 respectively. With only one part in 50,000, the bands at 517 and 616·5 disappear; the band 559—549 has a definite axis 549, whilst 580—564 becomes very narrow and has a definite axis 564. With one part in 100,000, the band 564 disappears, and 549 becomes practically a line, whilst with one part in 500,000 the only visible band is that at 681·5.

The principal band at 729—635 is continuous with one part in 10,000, but with one part in 50,000 it splits up into three bands; one, slender at 713—704, with its axis at 708·5; a second, somewhat stronger with its axis at 681·5, and a third, weaker at 659—650, with its axis at 654·5. The band at 681·5 is visible when the solution contains only one part in 500,000.

It follows that it is impossible to see all the absorption bands at once, since some disappear at the degree of dilution necessary to make the others distinguishable.

The method of successive dilutions is of great value in distinguishing chlorophylls from one another, and also in determining the exact effect of reagents, such as the splitting up of the principal band into three by the action of weak potassium hydroxide solution. C. H. B.

Coleopterin, a Pigment in the Elytræ of some Coleoptera. By ARTHUR BOWER GRIFFITHS (*Compt. rend.*, 1897, **124**, 1460—1461). —The elytræ of *Pyrochroa coccinea*, *Lina populi*, and *Coccinella septempunctata* contain a red, amorphous pigment soluble in alcohol, ether, carbon bisulphide, and acetic acid. It contains C, 45·86; H, 2·74, and N, 7·7 per cent., which corresponds with the formula $C_7H_5NO_5$. It is a lutein or a lipochrome, and the author gives it provisionally the name *coleopterin*. Its solutions show no definite absorption spectrum, but they are decolorised when exposed to light. C. H. B.

Phenylisindazole. By HENRI EUGÈNE CAUSSE (*Compt. rend.*, 1897, **124**, 505—506).—The product of the interaction of salicylaldehyde and phenylhydrazine melting at 142° has hitherto been regarded as a hydrazone, but the author finds that its composition and properties are those of a member of the isindazole group. It is prepared by adding to a well-cooled solution of phenylhydrazine (30 grams) and acetic anhydride (10 grams) in alcohol (150 c.c.) a solution of orthosalicylaldehyde (30 grams) also dissolved in alcohol (about 100 c.c.). The crystals which separate on cooling, after being dried and recrystallised from alcohol, are obtained as colourless, prismatic needles melting at 142° without undergoing decomposition, and having the formula $C_{13}H_{10}N_2$. They are insoluble in water, and only slightly soluble in alcohol, ether, and benzene in the cold, but are somewhat more so in these liquids on warming. Caustic alkalis are without action on the substance, ferric chloride gives no coloration, and Fehling's solution is not reduced. Heated in sealed tubes at 100° with acetic anhydride or benzoic anhydride, brown liquids are obtained from which the original substance can be recovered by treatment with caustic soda. Alkylic iodides are without action, and no nitroso-derivative is obtained by the action of nitrous anhydride. The production of phenylisindazole can be represented by means of the two following equations.

(i) $OH\cdot C_6H_4\cdot COH + NH_2\cdot NHPh = OH\cdot C_6H_4\cdot CH\colon N\cdot NHPh + H_2O$,

(ii) $OH\cdot C_6H_4\cdot CH\colon N\cdot NHPh = C_6H_4<{}^{-CH-}_{NPh}>N + H_2O$.

Parahydroxybenzaldehyde, when submitted to the same treatment as the ortho-derivative, does not yield any crystalline product, but in aqueous solution a crystalline substance is obtained melting at 179°, the composition of which is being studied by the author. A. C. C.

The Pyrazole Series. By LUIGI BALBIANO (*Gazzetta*, 1897, **27**, i, 415).—The author replies briefly to Claisen's criticism (this vol., i, 440) of the work of Balbiano and Severini (Abstr., 1893, i, 673), and states his intention of repeating the work in question. W. J. P.

Metallic Compounds of Pyridine and the Electrolysis of Pyridine. By FRITZ REITZENSTEIN (*Zeit. anorg. Chem.*, 1897, **15**, 192—193).—The author is engaged on the study of the hydrates, ammonia and pyridine compounds of bivalent metals. He gives a list of the metallic compounds of pyridine which he has prepared. These will be described later. Pincussohn, in his recent paper (this vol., i, 540), has evidently overlooked the author's work (*Annalen*, 1894, **282**, 270—280; *Zeit. anorg. Chem.*, 1896, **11**, 254—263).

E. C. R.

"Loretin"; Metiodorthohydroxyquinolineanasulphonic Acid. By ADOLF CLAUS and SIGISMUND BAUMANN (*J. pr. Chem.*, **55**, 457—480). —Several alkali earth salts of metiodorthohydroxyquinoline-anasulphonic acid, known as "loretin," are described.

Neutral calcium loretate, $(OH\cdot C_9NH_4I\cdot SO_3)_2Ca + 2\frac{1}{3}H_2O$ [$I : OH : SO_3 = 3 : 2 : 5$], crystallises in fiery red prisms, which lose $\frac{1}{3}H_2O$ at 100° without change of colour, and the other $2H_2O$ at 130°, changing to light yellow. Its aqueous solution is decomposed by sunlight at 60—70°, iodine being liberated. The *basic salt* is an anhydrous, cream-coloured compound crystallising in needles. *Neutral strontium loretate* forms orange-red prisms containing $1H_2O$, and the *basic salt* slender anhydrous needles. *Neutral barium loretate* consists of orange-red needles containing $2\frac{1}{2}H_2O$, the *basic salt* forming slender needles of a greenish-yellow colour, and containing $1H_2O$. *Neutral magnesium loretate*, best produced by treating "loretin" with magnesium carbonate, crystallises in prisms with $7H_2O$; the *basic salt* crystallises with $5H_2O$.

Two acids are produced by the decomposition of sodium loretate in boiling water. The first is evidently orthohydroxyquinolineanasulphonic acid, whilst the second, which is more soluble and can be separated from it by fractional crystallisation, consists of dark red prisms softening at 285°, and is probably an anhydrous compound of 1 mol. orthohydroxyquinolineanasulphonic acid with 1 mol. of 1 : 2-dihydroxyquinolineanasulphonic acid, the *neutral barium* salt consists of yellow, transparent plates, whilst the *acid salt* forms fiery red, glistening needles containing $9H_2O$, and the *basic salt* greenish-yellow crystals insoluble in cold water. J. F. T.

Derivatives of Isonarcotine: Hydrodicotarnine, a New Base. By E. BANDOW (*Ber.*, 1897, **30**, 1745—1749).—Attempts to resolve

isonarcotine into optical components by means of tartaric and racemic acids have, hitherto, been fruitless.

Hydrogen isonarcotine d-*tartrate* contains $3\frac{1}{2}H_2O$, and forms long, colourless needles melting at 180°; *hydrogen isonarcotine* l-*tartrate* also contains $3\frac{1}{2}H_2O$, and crystallises in white plates melting at the same temperature as the foregoing salt. *Hydrogen isonarcotine racemate* is almost insoluble in cold water, and crystallises in small, white needles.

Isonarcotine *ethiodide* is readily soluble in water and alcohol, and forms small, white crystals melting at 183°; the *ethochloride* is amorphous, and yields an orange *platinochloride.* The *ethylhydroxide* is very deliquescent, and with concentrated sulphuric acid does not give the red coloration characteristic of the original base. Although an aqueous solution of narcotine ethylhydroxide undergoes spontaneous conversion into ψ-homonarceine, neither the ethylhydroxide nor the methylhydroxide of isonarcotine exhibits the corresponding change, the unaltered substances being recovered on evaporating the aqueous solutions. Isonarcotine *methiodide* forms small, white needles, and melts at 212°; the *platinochloride* of the methochloride has been analysed; the *methylhydroxide* is very hygroscopic.

Hydrodicotarnine, $C_{24}H_{28}N_2O_6$, is prepared by heating hydrocotarnine with 73 per cent. sulphuric acid for half an hour at about 80°; it is also produced when the base is dissolved in cold 82 per cent. sulphuric acid, when the temperature rises spontaneously to 60°. It is insoluble in ammonia, and somewhat sparingly soluble in benzene, but dissolves readily in alcohol or chloroform; it crystallises in small, bright yellow needles, and melts at 211°. The *hydrobromide* forms white needles melting at 218—220°, and the *hydriodide* is yellowish and melts at 227—229°; the *platinochloride* is orange-yellow.

A table comparing the properties and derivatives of hydrodicotarnine with those of the closely related cotarnine and hydrocotarnine is included in the paper. M. O. F.

Pilocarpine and Pilocarpidine. By AUGUSTE PETIT and MAX POLONOWSKY (*J. Pharm.*, 1897, [vi], 5, 370—375, 430—437, and 475—483. Compare Hardy and Calmels, *Compt. rend.*, **102**, 1116, 1251, and 1562).—Paul and Cownley have already pointed out (*Pharm. J. Trans.*, July and November, 1896) that different specimens of commercial pilocarpine and its derivatives differ largely, not only in their physical properties, but also in their physiological action. The authors have therefore undertaken the study of the two alkaloids, pilocarpine and pilocarpidine, and of their derivatives. These two compounds are easily separated from the other bases which occur in jaborandi leaves, since they both combine with alkali hydroxides, yielding compounds which are insoluble in chloroform or ether. The best method for separating the two is by fractional crystallisation of their hydrochlorides from alcohol. A simple method for converting pilocarpine into pilocarpidine is to heat the base or one of its salts with an alcoholic solution of sodium ethoxide on a water bath.

The following table gives a *résumé* of the chief properties of the two alkaloids and their salts :—

	Pilocarpine.	Pilocarpidine.
Free base	Thick syrup, $[\alpha]_D$ in aqueous solution $= +106°$; in the presence of soda, $[\alpha]_D = +23·8°$.	Deliquescent prisms, $[\alpha]_D = +50°$; in presence of soda, $[\alpha]_D = -3°$.
Nitrate	Prisms. Soluble in 7 parts of water at 18°, and in 146 parts of alcohol (95 per cent.) at 18°. Melting point 177—178°. $[\alpha]_D = +82·2°$.	Plates. Soluble in 8 parts of water, or 135 parts of alcohol. Melting point 158°. $[\alpha]_D = +38·5°$.
Hydrochloride	Anhydrous prisms. Soluble in 0·4 part of water, or in 10 parts of alcohol. Melting point 200°. $[\alpha]_D = +91°$.	Flakes containing water of crystallisation. Soluble in 0·27 part of water, or in 2 parts of alcohol. Melting point of the hydrated salt = 124°, and of the anhydrous salt = 161°. $[\alpha]_D = +37·3°$.
Hydrobromide	Prisms. Melting point 178°. $[\alpha]_D = +76°$.	Needles. Melting point 143°. $[\alpha]_D = +32·6°$.
Salicylate	Melting point 120°. $[\alpha]_D = +62·5°$.	Melting point 99°. $[\alpha]_D = +30°$.
Picrate	Hard needles. Melting point 159—160°.	Silky needles. Melting point 160—161°.
Sulphate	Small needles. Melting point 120°. $[\alpha]_D = +86°$.	Not been prepared.
Acid aurochloride	Yellow needles melting at 100°, or when anhydrous at 130°.	Anhydrous needles. Melting point 160°.
Modified aurochloride	Melting point 167°.	Melting point 190°.
Iodomethoxide	Not been prepared.	Prisms. Melting point 108°. $[\alpha]_D = +26°$.

The authors find that the impurities in commercial pilocarpine salts are the corresponding pilocarpidine compounds; in the case of the nitrate, the latter sometimes amounts to 50 per cent. The authors also think that the pilocarpidine exists ready formed in the plant, and is not produced from pilocarpine during the process of extraction (compare Hardy and Calmels). The pilocarpic and pilocarpidic acids which Hardy and Calmels believed to be hypothetical compounds, of which pilocarpine and pilocarpidine might be regarded as the anhydrides, have actually been obtained by the authors. Sodium pilocarpate is formed when pilocarpine dissolves in caustic soda; this may be transformed into the barium salt, and when the latter is treated with the requisite quantity of sulphuric acid, and the filtrate allowed to evaporate spontaneously, free *pilocarpic acid* is obtained in the form of a syrup. It is readily soluble in water or alcohol, but insoluble in ether, chloroform, or benzene, $[\alpha]_D = +23·8°$. It gradually loses water when heated, and more rapidly on the addition of acids, even if dilute, being reconverted into pilocarpine. *Pilocarpidic acid* resembles the above acid in all its properties except that it is lævogyrate. The following constitutional formulæ are suggested for the two alkaloids:—

Pilocarpine.	Pilocarpidine.
$C_5NH_4\cdot CMe<\begin{matrix}COO\\NMe_3\end{matrix}>$	$C_5NH_4\cdot CMe<\begin{matrix}COOH\\NMe_2\end{matrix}$

J. J. S.

Isomerism of Pilocarpine and Pilocarpidine. By AUGUSTE PETIT and MAX POLONOWSKY (*J. Pharm.*, 1897, [vi], **6**, 8—11. Compare preceding abstract).—The authors now show that pilocarpine is isomeric with pilocarpidine, and that it cannot have the constitution suggested by Hardy and Calmels, since, when transformed into pilocarpidine, it yields no methylic alcohol. The transformation may be brought about by boiling pilocarpine or one of its salts with sodium ethoxide or with an aqueous solution of sodium hydroxide. Pilocarpine hydrochloride is also quantitatively converted into pilocarpidine hydrochloride when heated for a few minutes just above its melting point.

Pilocarpine platinochloride, $C_{11}H_{16}N_2O_2,H_2PtCl_6$, crystallises from boiling water in large, orange plates. 0·8 part of the salt dissolves in 100 parts of water at 23°. Its melting point is 213°.

Pilocarpidine platinochloride is much less soluble in boiling water than its isomeride, but resembles it in crystalline form; it melts at 222—224°. Hardy and Calmels describe this compound as containing water of crystallisation and as melting at 130°, whilst Merck gives the melting point as 183—190°. J. J. S.

Two New Alkaloids isolated from a Species of Jaborandi. By AUGUSTE PETIT and MAX POLONOWSKY (*J. Pharm.*, 1897, [vi], **5**, 369—370).—The authors have isolated two new alkaloids from Holme's *Aracati Jaborandi*, *Pilocarpus spicatus*. The leaves are extracted in the usual way, and the mixture of bases obtained converted into nitrates. The mixed nitrates are then treated with sodium hydroxide and extracted with chloroform. After evaporating the chloroform, an alkaloid, *ψ-jaborine*, is obtained as a colourless oil with strongly alkaline properties and readily soluble in water, alcohol, or chloroform. It is optically inactive, and yields a *nitrate* which crystallises in large, thin plates melting at 158°, and a *hydrochloride* which forms small, hard prisms and melts at 222°. The second alkaloid, *ψ-pilocarpine*, has very much the same properties as pilocarpine, except that it is optically inactive. Its *nitrate* crystallises in small needles melting at 142°, and is more readily soluble in alcohol than ψ-jaborine nitrate. Its *hydrochloride* forms small prisms sparingly soluble in alcohol or water, and melts at 198—199°. J. J. S.

New Reaction of Eserine. By A. J. FERREIRA DA SILVA (*Zeit. anal. Chem.*, 1897, **36**, 540; from *Pharm. Zeit. für Russland*, **32**, 629).—Eserine and its salts, dissolved in fuming nitric acid, give yellow solutions which, when warmed on the water bath, become darker and leave a green residue. The latter dissolves with a green colour in water and strong alcohol; dissolved in dilute nitric acid, the solution fluoresces greenish-yellow by transmitted light, blood-red by reflected light. The absorption spectrum differs from those of physostygmine and rubreserine. M. J. S.

Action of Iodine on Proteids. By E. Lépinois (*J. Pharm.*, 1897, [vi], 5, 561—566).—A solution of iodine is added to milk until, at the end of 24 hours, free iodine can still be detected by agitation with chloroform. At the end of this time, the mixture is poured into an equal volume of water containing a small quantity of acetic acid, and the brown coagulum thus obtained is washed first with water by decantation, and then with dilute caustic soda, which dissolves the iodocasein. The filtered liquid is precipitated by means of acetic acid, the operations of solution and precipitation being repeated five or six times, when the *iodocasein* is obtained in a pure form. After washing with water, alcohol, and ether, and drying, it is obtained as a slightly yellow, amorphous powder containing 21·6 per cent. of iodine and 14·15 per cent. of nitrogen. When heated, it melts and then carbonises. It is readily soluble in acetic acid, and in potassium, sodium, and ammonium hydroxides or carbonates, but is insoluble in alcohol, ether, chloroform, and water. None of these solvents withdraw any of its iodine, and the percentage of iodine remains constant after repeated solution and precipitation. The therapeutic properties of the substance are being examined. J. J. S.

Organic Chemistry.

Synthesis and Constitution of Isoprene. By WILHELM EULER (*Ber.*, 1897, **30**, 1989—1991).—3-Methylpyrrolidine has been subjected to the same series of reactions as Ciamician and Magnaghi (Abstr., 1885, 1242) performed with pyrrolidine itself. 3-Methylpyrrolidine, $\begin{matrix} CH_2\text{—}CH_2 \\ | \\ CHMe\cdot CH_2 \end{matrix}\!\!>NH$, if treated with methylic iodide, yields a compound, $\begin{matrix} CH_2\text{—}CH_2 \\ | \\ CHMe\cdot CH_2 \end{matrix}\!\!>NMe_2I$, which, when distilled with potash, yields 2 : 3 : 5-trimethylpyrrolidine, $\begin{matrix} CH_2\text{—}CHMe \\ | \\ CHMe\cdot CHMe \end{matrix}\!\!>NH$. This again unites with methylic iodide, yielding a compound, $\begin{matrix} CH_2\text{—}CHMe \\ | \\ CHMe\cdot CHMe \end{matrix}\!\!>NHMeI$, which, when distilled with potash, yields trimethylamine and an unsaturated hydrocarbon, $CH_2{:}CH\cdot CMe{:}CH_2$; the latter boils at 33—39°, and forms, with hypochlorous acid, a product, $C_5H_{10}O_2Cl_2$, melting at 80—81°, and identical with that obtained by the action of the same acid on isoprene (Mokiewsky, *Chem. Zeit.*, 1895, No. 101). It must therefore be isoprene, to which, then, the above constitution must be assigned. C. F. B.

Compounds of Mercuric Cyanide with Metallic Haloids. By RAOUL VARET (*Ann. Chim. Phys.*, 1896, [vii], **8**, 240—288, and 437—438).—The first section of this paper deals with the thermochemistry of the compounds of mercuric cyanide with a number of metallic haloids. In the first chapter of this section, the heats of formation of compounds of mercuric cyanide with the iodides of sodium, ammonium, lithium, barium, strontium, calcium, magnesium, and cadmium are given (Abstr., 1896, ii, 148); in the second chapter, the heats of formation of the corresponding bromocyanides (Abstr., 1896, ii, 88), and in the third the heats of formation of the corresponding chlorocyanides (Abstr., 1896, i, 3). In the second section of this paper, the author describes experiments made with the object of distinguishing cyanogen combined with mercury from cyanogen combined with the other metals above referred to, in order that some light might be thrown upon the constitution of the double salts in question. The third section deals with the application of these methods and the conclusions arrived at (Abstr., *loc. cit.*). A. C. C.

Magnesium Methylic Carbonate and Sulphite. By EMERICH SZARVASY (*Ber.*, 1897, **30**, 1836—1838).—If magnesium methoxide (this vol., i, 309) is suspended or dissolved in methylic alcohol, and carbonic anhydride passed in, a clear solution is obtained, and after the alcohol has been evaporated *magnesium methylic carbonate*, $(OMe\cdot COO)_2Mg$, remains as a white, amorphous powder. When a methyl alcoholic solution of this substance is treated with a few drops of water, a gelatinous precipitate forms; this redissolves when more

water is added, but the solution, when boiled, deposits magnesium carbonate, and is found to contain methylic alcohol. Acids decompose the compound with evolution of carbonic anhydride, a magnesium salt and methylic alcohol being formed in addition.

If sulphurous, instead of carbonic, anhydride is employed, or if sulphurous anhydride is passed into the solution of the methylic carbonate in methylic alcohol, *magnesium methylic sulphite*, $(OMe\cdot SOO)_2Mg$, is formed. This is exactly analogous to the carbonate in its properties and reactions. C. F. B.

Separation of Methylamines. By MARCEL DELÉPINE (*Ann. Chim. Phys.*, 1896, [vii], 8, 439—465).—A new method is described for the separation in a state of purity of the methylamines (Abstr., 1896, i, 519), and the properties of some of their salts and derivatives are given (Abstr., 1896, i, 588). Trimethylamine hydriodide crystallises in large, colourless plates melting at about 260° to a red liquid, and is not deliquescent. Methylamine may be conveniently separated as the bismuthoiodide described by Kraut, the base being obtained from it by treatment with caustic alkalis. A. C. C.

Action of Dichlorethylamine on Ethylamine. By EDUARD LIPPMANN and CARL REGENSDORFER (*Ber.*, 1897, 30, 2053—2057).—Dichlorethylamine prepared by Tscherniak's method (*Ber.*, 1876, 9, 146) was added drop by drop to thoroughly dried ethylamine placed in a freezing mixture of ice and salt. At the end of 24 hours, the clear liquid was decanted from the crystals of ethylamine hydrochloride, the latter being well washed with ether until the ethereal extract no longer gave a precipitate with silver nitrate. After the ether and ethylamine had been carefully distilled off on the water bath, a product was obtained which distilled at 35—39° under a pressure of 10 mm. As it still contained some dichlorethylamine, it was treated with aluminium amalgam according to H. Wislicenus's method, and the fraction distilling at 35—37° was then found to be free from chlorine. This fraction, which consists of pure *ethyldiethylidenediamine*, $NEt<{CHMe \atop CHMe}>NH$, is a colourless oil with an odour resembling that of camphor. It reduces warm ammoniacal silver nitrate and warm mercuric chloride solutions, but not Fehling's solution; water has no action on it, but acids hydrolyse the compound, yielding ammonia, aldehyde, ethylamine, and ethylhydroxylamine (or diethylhydroxylamine), if hydrochloric or oxalic acid is used. No alkylhydroxylamine is formed when sulphuric acid is used as the hydrolysing agent. J. J. S.

Amido-alcohols of the Fatty Series. By OSCAR PILOTY and OTTO RUFF (*Ber.*, 1897, 30, 2057—2068. Compare this vol., i, 453). —*Hydroxylamidodihydroxyisobutane* (2-methyl-2-hydroxylaminopropandiol-1 : 3), $CMe(NH\cdot OH)(CH_2\cdot OH)_2$, is obtained when Henry's tertiary nitroisobutylglycol (10 grams) is reduced with 2·5 per cent. sodium amalgam (285 grams) at 0° in the presence of crystallised aluminium sulphate (34·4 grams) and water (300 c.c.). The product is a syrup which solidifies within 1—2 days, and when crystallised from a mixture of alcohol and ether yields flat prisms melting at

122—123° (corr.). It is readily soluble in water or alcohol, but only sparingly in ether or benzene; it reduces Fehling's solution in the cold, and has basic properties. The *picrate*, $C_4H_{11}NO_3,C_6H_2(NO_2)_3\cdot OH$, crystallises from a mixture of alcohol and light petroleum in yellow, prismatic needles melting at 134°; it is readily soluble in water or alcohol, moderately in ethylic acetate, and sparingly in ether or benzene. The *oxalate*, $(C_4H_{11}NO_3)_2,C_2H_2O_4$, crystallises from alcohol in thick, quadratic prisms melting at 95—96°, and decomposing at about 100°. It is readily soluble in water, and sparingly in ethylic acetate, but insoluble in ether or benzene.

Hydroxyacetoxime, $OH\cdot N:CMe\cdot CH_2\cdot OH$, is obtained when the hydroxylamine compound is oxidised with mercuric oxide. It was only obtained in the form of a syrup, but was identified by conversion into methylglyoxalosazone which Pechmann (Abstr., 1887, 1103) and Laubmann (Abstr., 1888, 366) have already prepared. Hydroxyacetoxime is obtained in a crystalline form when pure acetylcarbinol (hydroxyacetone) is treated with an alcoholic solution of hydroxylamine. It crystallises from chloroform in prisms melting at 71° (corr.), is readily soluble in water, alcohol or ether, moderately in hot chloroform, and sparingly in benzene.

The aliphatic amido-alcohols obtained by the reduction of the nitro-compounds or of the oximes are stable substances. Their salts are readily soluble in water and in some cases extremely hygroscopic; the sulphates and oxalates are sparingly soluble in absolute alcohol, and can therefore be made use of for isolating the bases.

Amidoglycerol (2-aminopropandiol-1 : 3), $CH(CH_2\cdot OH)_2\cdot NH_2$, which has only been obtained in aqueous solutions, possesses strong alkaline properties, and is capable of dissolving lead hydroxide and the oxides of copper and silver. It does not reduce Fehling's solution even on boiling. Its *hydrochloride* is formed together with ammonia and isopropylamine by the reduction of dihydroxyacetoxime (this vol., i, 453). The *sulphate*, which is so hygroscopic that it can be obtained in the crystalline form only from absolute alcohol, crystallises in compact plates. The *oxalate* crystallises from dilute alcohol in plates decomposing at 200°. *Trihydroxytertiarybutylamine* (2-methylol-2-aminopropandiol-1 : 3), $C(CH_2\cdot OH)_3\cdot NH_2$, is obtained in the form of its *hydriodide* when tertiary nitroisobutylglycerol is reduced with hydriodic acid and yellow phosphorus. The salt crystallises from alcohol in strongly refractive crystals, $C_4H_{11}NO_3,HI+\frac{1}{2}C_2H_5\cdot OH$, melting at 105°; they rapidly effloresce on exposure to the air, and when dried melt at 188—189°. The free *base*, which is best obtained by treating the hydriodide with lead hydroxide, crystallises from its aqueous or alcoholic solution in long, compact needles melting at 167—168°; it is readily soluble in alcohol or water, sparingly in acetone, and practically insoluble in ether. It dissolves the hydroxides of lead, silver or copper, but not aluminium hydroxide, and it does not reduce Fehling's solution. The *hydrochloride* obtained when nitroisobutylglycerol is reduced with tin and hydrochloric acid, crystallises from alcohol in strongly refractive, six-sided plates, melting at about 149°, and decomposing at about 230°. The *sulphate* crystallises in thin, six-cornered plates melting at 167°. The *oxalate* crystallises in needles which decompose at 188°. The

compounds with gold chloride, potassium, bismuthoiodide and also with picric acid are extremely readily soluble in alcohol. Sodium nitrite reacts with an aqueous solution of the hydrochloride yielding the nitrite of the base, and when this is warmed, gas is evolved and an oily substance, probably the alcohol, can be extracted from the residue. A *triacetyl* derivative of the hydrochloride, namely,

$$C(CH_2{\cdot}OAc)_3{\cdot}NH_2,HCl,$$

is obtained together with the *tetracetyl* derivative, $C(CH_2{\cdot}OAc)_3{\cdot}NHAc$, when the hydrochloride (5 grams) is heated on the water bath for 6 hours with acetic anhydride (15 grams) and glacial acetic acid (20 grams). The triacetyl derivative crystallises in thin, elastic needles, or in compact, rhombic prisms melting at 132—133°. It is readily soluble in water, alcohol, ethylic acetate, or acetone, sparingly in benzene and almost insoluble in ether, or light petroleum. When treated with sodium nitrite, an oil which is sparingly soluble in water, and which the authors regard as impure *triacetoxyisobutane* is formed. This oil, when distilled under diminished pressure, is converted into acetic acid and a *diacetyl* derivative of an *inner anhydride of isobutylglycerol* (trihydroxyisobutane), $(CH_2{\cdot}OAc)_2C{<}{\overset{CH_2}{\underset{O}{|}}}$ which distils at 174—176° under a pressure of 20 mm. This compound, tetracetylmethylolaminopropandiol, $C(CH_2{\cdot}OAc)_3{\cdot}NHAc$, is readily soluble in ether, alcohol, and benzene, and may be salted out from its aqueous solutions. It does not combine with hydrogen chloride, and crystallises from water in broad prisms melting at 114—115°.

Tertiary isobutylglycolamine (2-methyl-2-aminopropandiol-1 : 3), $CMe(CH_2{\cdot}OH)_2{\cdot}NH_2$, is obtained in the form of its hydrochloride by the reduction of nitroisobutylglycol with tin and hydrochloric acid. The *hydrochloride*, $C_4H_{11}NO_2,HCl$, which crystallises from a mixture of alcohol and ether in prismatic needles melting at 91—92°, is extremely hygroscopic, and dissolves readily in alcohol, but is insoluble in ether. The *sulphate* crystallises in pointed needles decomposing at about 225°, it is extremely hygroscopic, but is practically insoluble in cold alcohol. The *oxalate* crystallises from alcohol in flat, rhombic needles which decompose at about 215°. It dissolves readily in water, but is not hygroscopic. The free base is obtained in the form of a syrup by the action of lead hydroxide or silver oxide on the base, it cannot be completely dried over sulphuric acid, and when distilled under a pressure of 16·5 mm. the greater part is decomposed but yields a small quantity of crystals melting at 60—95°. The strongly alkaline solution dissolves cupric hydroxide, silver oxide, and to a certain extent silver chloride, but it does not reduce Fehling's solution.

J. J. S.

The Double Aldehyde of Suberic Acid. By ADOLF VON BAEYER (*Ber.*, 1897, **30**, 1962—1965).—The ease with which α-hydroxypinic acid is converted by lead peroxide into the aldehyde-acid containing 1 carbon atom less than itself, seemed to show that this reaction might be generally applicable, and it was found that dihydroxysebacic acid, prepared from the dibromo-acid by treatment with silver oxide, gave the *dialdehyde of suberic acid*, $CHO{\cdot}[CH_2]_6{\cdot}CHO$, when treated

with lead peroxide; during the process of oxidation, however, it was necessary to have a strong acid present, in order to prevent the formation of a lead salt of the acid, and for this purpose phosphoric acid was found to be the most serviceable. The dialdehyde distils, with partial decomposition, at 230—240°, but if kept, quickly polymerises to a hard, vitreous mass. Its aqueous solution smells like oenanthaldehyde and shows all the reactions of an aldehyde, forming a *hydroxylamine* compound which crystallises from alcohol in prisms melting at 150—155°, also a *semicarbazone* melting at 183—185°. On oxidation with permanganate, it is converted into suberic acid. J. F. T.

Methyl Derivatives of Acetylmethyl Hexyl Ketone (2:4-Decadione). By J. KRAMERS (*Rec. Trav. Chim.*, 1897, **16**, 116—125).—Claisen and Ehrhardt (*Ber.*, **22**, 1016) have demonstrated that, when an acetyl group is introduced into methyl propyl ketone, it enters the methyl and not the propyl group, and proved this by showing that the condensation product of ethylic butyrate and acetone is acetylmethyl propyl ketone (2 : 4-heptadione), and is identical with the product of the action of ethylic acetate on methyl propyl ketone. The author has proved this by another means, using methyl hexyl ketone.

If it be admitted that the condensation of methyl hexyl ketone with ethylic acetate can only take place in one of the following ways,

$$\text{(I)}\ CH_3\cdot COOEt + CH_3\cdot CO\cdot C_6H_{13} = CH_3\cdot CO\cdot CH_2\cdot CO\cdot C_6H_{13} + Et\cdot OH$$
$$\text{(II)}\ CH_3\cdot COOEt + CH_3\cdot CO\cdot CH_2\cdot C_5H_{11} = CH_3\cdot CO\cdot CH(C_5H_{11})\cdot CO\cdot CH_3 + Et\cdot OH,$$

it is evident that the product from I has 2 atoms of hydrogen capable of being replaced by alkyl groups, whilst that of II has only one.

The author has succeeded in preparing both the mono- and dimethyl-derivatives of acetylmethyl hexyl ketone, and finds, in contradistinction to what Claisen says, that the monomethyl derivative gives, at once, a compound with copper acetate of a dirty green colour, whilst the copper derivative of the nonmethylated diketone is violet-blue, and the dimethylated diketone gives no copper derivative at all.

A common property of all compounds containing the grouping $R\cdot CO\cdot CHR\cdot COR$, except malonic acid and its derivatives, is the production of a dark red coloration with an alcoholic solution of ferric chloride; the above-mentioned diketone and its monomethyl derivative give this characteristic reaction, whilst with the dimethylated diketone only a feeble yellowish colour is obtained.

The author has tried the action of potash on the monomethyl derivative, but the amount of material at his disposal was insufficient to satisfactorily prove where fission takes place with this ketone.

Acetylmethyl hexyl ketone, prepared by the action of ethylic acetate on methyl hexyl ketone, is a colourless liquid boiling at 130—131° under a pressure of 23 mm., and solidifying at $-6°$. It has a specific gravity of 0·913 at 15°, and the molecular weight, as determined by Beckmann's method, is 157, instead of 170 as required by the formula $C_{10}H_{18}O_2$.

Monomethyl acetylmethyl hexyl ketone (3-methyldecadione-2 : 4 or

α-acetylethyl hexyl ketone, $COMe{\cdot}CHMe{\cdot}CO{\cdot}C_6H_{13}$), is obtained by the action of methylic iodide on the diketone. It is a colourless liquid with a peculiar odour, boiling at 143—144° under a pressure of 23 mm.; it does not solidify at a temperature of −40°. It has a specific gravity = 0·916 at 15°, and a molecular weight of 170 (calculated 184).

Dimethyl acetylmethyl hexyl ketone (dimethyl-3-decadione-2 : 4, α-acetylisopropyl hexyl ketone), $COMe{\cdot}CMe_2{\cdot}CO{\cdot}C_6H_{13}$, prepared by the action of methylic iodide on the monomethyl derivative, is a colourless, peculiar-smelling liquid boiling at 142·5—143·5° at a pressure of 18 mm., and does not solidify at −40°. Its specific gravity = 0·912 at 15°, and the molecular weight is 180 (calculated 198). A. W. C.

δε-Heptenoic Acid. By Fritz Fichter and Eugen Gully (*Ber.*, 1897, **30**, 2047—2050).—δε-Unsaturated acids can be obtained by a method similar to that previously used for the preparation of γδ-unsaturated acids (this vol., i, 13). *Ethylic acetyladipate*, $COOEt{\cdot}CHAc{\cdot}[CH_2]_3{\cdot}COOEt$, obtained by the action of ethylic γ-chlorobutyrate on ethylic sodioacetoacetate, distils at 160° under a pressure of 12 mm. The ethylic salt, when subjected to ketonic hydrolysis, yields Perkin's ω-acetylvaleric acid (Trans., 1890, 229) whilst acid hydrolysis gives rise to adipic and acetic acids. When ethylic acetyladipate is reduced with aqueous alcohol and sodium amalgam (4 per cent.) and the solution kept neutralised as far as possible with hydrochloric acid, the chief products are adipic acid and *ε-hydroxy-α-ethyladipic acid*, $COOH{\cdot}CH(CHMe{\cdot}OH){\cdot}[CH_2]_3{\cdot}COOH$; these can be separated by means of chloroform in which adipic acid is insoluble. The new acid was obtained as a syrup; but its *barium*, *calcium*, and *silver* salts were prepared and analysed. When distilled, the acid decomposed into carbonic anhydride, water, ethylideneadipic acid, and δε-heptenoic acid. *Ethylideneadipic acid*, $CHMe{:}C(COOH){\cdot}[CH_2]_3{\cdot}COOH$, crystallises from water, melts at 130°, and is not volatile with steam. *δε-Heptenoic acid*, $CHMe{:}CH{\cdot}[CH_2]_3{\cdot}COOH$, is readily volatile with steam, and is isomeric with Schmidt's acid (*Annalen*, **255**, 77). The *calcium* salt crystallises with $1H_2O$, but the *cadmium* and *silver* salts are anhydrous. The acid combines with bromine, yielding an oily *dibromide*, and with hydrogen bromide, yielding an oily *hydrobromide*, which, when boiled with water, is converted into *δ-hydroxyheptoic acid.* The *barium* salt of the hydroxy-acid is readily soluble in water, and melts at 80—90°; the *silver* salt is obtained as a colourless precipitate. The free hydroxy-acid, when boiled with hydrochloric acid, is partially converted into a *δ-lactone*, which, however, readily passes back again into the acid. J. J. S.

α-Hydroxy-α-methyladipic Acid and δε-Hexenoic Acid. By Fritz Fichter and Werner Langguth (*Ber.*, 1897, **30**, 2050—2053). —*α-Hydroxy-α-methyladipic acid*, $COOH{\cdot}CMe(OH){\cdot}[CH_2]_3{\cdot}COOH$, is obtained by the hydrolysis of the nitrile formed by the action of potassium cyanide and hydrochloric acid on Woulff's acetobutyric acid (*Annalen*, **216**, 130). It crystallises from a mixture of ether and light petroleum in small needles melting at 92°. The *silver* salt is an amorphous precipitate, and the *alkaline earth* salts are readily soluble

in water. When heated for some time at 100° the acid yields the corresponding lactonic acid, *hexo-δ-lactone-δ-carboxylic* acid, which is extremely hygroscopic and unstable.

When distilled in small portions, α-hydroxy-α-methyladipic acid yields a small quantity of the lactone, together with a non-volatile dibasic unsaturated *acid*, $C_7H_{10}O_5$, melting at 153°, and about equal quantities of γδ- and δε-hexenoic acids, both of which are volatile with steam. These two acids are most conveniently separated by means of their barium salts, the barium salt of the γδ-acid being practically insoluble in alcohol (this vol., i, 13), whereas the isomeric salt is readily soluble. *δε-Hexenoic acid* boils at 202—204°, and does not solidify in a freezing mixture. The *barium* salt is anhydrous, and is readily soluble in alcohol or water; the *calcium* salt is also readily soluble, and crystallises with $1H_2O$. The *cadmium* and *silver* salts are amorphous. The acid readily combines with hydrogen bromide, and when the compound thus formed is boiled with water, Woulff's capro-δ-lactone (hexo-δ-lactone) is obtained (*Annalen*, **216**, 135). J. J. S.

Castor Oil. By Hans Meyer (*Arch. Pharm.*, 1897, **235**, 184—191).—In reference to Juillard's observation (Abstr., 1895, i, 500) that dihydroxystearic acid is contained in castor oil, the author states that he had also isolated this compound at the time of his previous research (*Arch. expt. Path. Pharm.*, 1890, **28**, 145) by the action of dilute hydrochloric acid on the purified calcium salt prepared by Claus's method. The ethereal solution, after washing and standing, deposits crystalline leaflets which melt at 140—141°, and closely resemble cholesterol. They are, however, insoluble in ether, and do not form an additive compound with bromine. Analysis indicates an empirical formula, $C_{18}H_{36}O_4$. From 2 kilograms of oil, 1·5 grams of pure substance are obtained. Attempts to prepare this compound by heating ricinoleic acid with water at 300°, or with sodium hydroxide solution at 200°, failed.

Juillard found that the triglyceride of ricinoleic acid could not be prepared by Berthelot's method owing to the polymerisation of the acid, whereby a glyceride of polyricinoleic acid was produced. The author finds that preparations of the pure acid which originally had a sp. gr. = 0·9460 at 12°, after a lapse of eight years had become more viscous, of a sp. gr. = 0·9680 at 12°, and required about one-third less alcoholic potassium hydroxide solution for neutralisation. Hübl's iodine number was also found to have diminished from 85·53 for the freshly prepared acid to 64·06. The specific gravity, saponification number, and molecular refraction agree with the numbers calculated on the assumption that these old preparations are a mixture of 30 parts of ricinoleic acid with 70 parts of diricinoleic acid. By the action of alcoholic potash, ordinary ricinoleic acid may be obtained.

The author has succeeded in preparing the triglyceride of ricinoleic acid by passing a slow stream of carbonic anhydride into a mixture of the acid with glycerol, and heating at 280—300°. The product, freed from excess of glycerol by the addition of water, forms an almost colourless neutral oil possessing the same viscosity, taste, and physiological action as castor oil. It dissolves in 96 per cent. alcohol and in methylic alcohol, whereas Juillard's glycerides of polyricinoleic acid

only partially dissolve. The saponification number agrees with that of the triglyceride. The sp. gr. of two preparations was 0·959 and 0·984 respectively, whilst that of ordinary castor oil is 0·95 to 0·97, and that of the oil freed from stearates by cooling to +5° is 0·9635 at 15°. Specific rotatory power $[\alpha]_D = +5·16°$; for castor oil $[\alpha]_D = +4·68°$. Hübl's iodine number = 71—86·4, the calculated number for the pure triglyceride being 81·62, whilst that of ordinary castor oil is 84·0—84·7. The synthetically prepared oil, unlike the ordinary oil, does not form solid ricinelaidine by the action of nitrous acid, but only becomes more viscous.

The sp. gr. of triglyceride preparations which had been kept eight years was found also to have increased, in one case to 0·9980 at 14·5°, in another to 1·009. The numbers calculated from Traube's constants for the simple formula $C_{57}H_{104}O_9$, are 0·995 for the double formula, and 1·000 for the treble, hence polymerisation has evidently taken place. This must have been effected by simple physical association of the molecules, or more probably by union with disappearance of the double bonds, for condensation between carboxyl and hydroxyl groups as in the case of the free acid, is here impossible. The iodine number was also found to have become less. The author regards Juillard's preparation, which is stated to be a mixture of two molecular proportions of triricinolein with one of diricinolein, as the nearly pure diglyceride of ricinoleic acid, with which assumption Juillard's saponification number very nearly agrees; he thinks that the determination of the molecular weight by Raoult's method may have been vitiated by polymerisation of the glyceride. E. W. W.

Hydroxymethylene Compounds. By LUDWIG CLAISEN (*Annalen*, 1897, **297**, 1—98. Compare Abstr., 1894, i, 66, and 1895, i, 62).—*Methylic ethoxymethyleneacetoacetate*, OEt·CH:CAc·COOMe, is prepared by heating methylic acetoacetate with ethylic orthoformate and acetic anhydride in a reflux apparatus (compare *loc. cit.*); it boils at 173—174° under a pressure of 45 mm., and slightly decomposes when it is distilled under the ordinary pressure at 265—268°.

Ethylic methoxymethyleneacetoacetate, OMe·CH:CAc·COOEt, is prepared from the silver derivative of ethylic hydroxymethyleneacetoacetate and methylic iodide; it boils at 150—152° under a pressure of 19 mm; the *methylic* salt, obtained from methylic acetoacetate, methylic orthoformate, and acetic anhydride, boils at 150° under a pressure of 16 mm.

Although ethylic hydroxymethyleneacetoacetate is produced when the ethoxy-compound is treated with water, it is more conveniently prepared by agitating the substance with a concentrated, aqueous solution of copper acetate, which gives rise to the *copper* derivative of ethylic hydroxymethyleneacetoacetate; the *potassium, barium, calcium, magnesium,* and *silver* derivatives are anhydrous, and the *ammonium* derivative melts at 104—105°.

Methylic hydroxymethyleneacetoacetate, OH·CH:CAc·COOMe, prepared by the action of aqueous copper acetate on the corresponding ethoxy-compound, has a sp. gr. = 1·186 at 15°, and boils at 110° and 185° under pressures of 57 mm. and 750 mm. respectively. The

copper derivative crystallises from methylic alcohol in lustrous leaflets, and melts at 207—208°.

When ethylic hydroxymethyleneacetoacetate is hydrolysed with the calculated quantity of a boiling, normal solution of caustic soda, ethylic acetoacetate and sodium formate are produced; boiling water alone gives rise to triacetylbenzene, hydroxymethyleneacetone being formed as an intermediate compound. Oxidation of ethylic hydroxymethyleneacetoacetate with silver nitrate resolves it into ethylic acetoacetate and carbonic anhydride.

Ethylic amidomethyleneacetoacetate, $NH_2 \cdot CH{:}CAc \cdot COOEt$, prepared by the action of alcoholic ammonia on ethylic ethoxymethyleneacetoacetate, crystallises in beautiful, colourless plates, melts at 55°, and boils at 176—179° under a pressure of 15 mm. The compound behaves like an amide, and forms a *potassium* derivative, which yields ammonia when heated in aqueous solution; the *copper* derivative crystallises from alcohol in bluish-violet scales, and melts and effervesces at 195—198°. The *benzoyl* derivative is prepared by the action of benzoic chloride on the base, and also by heating ethylic ethoxymethyleneacetoacetate with benzamide at 150°; it crystallises from alcohol in pale yellow needles and prisms, and melts at 95°. The *acetyl* derivative forms long, colourless needles, and melts at 88°. The *carbamide* derivative, $NH_2 \cdot CO \cdot NH \cdot CH{:}CAc \cdot COOEt$, obtained by heating ethylic ethoxymethyleneacetoacetate with carbamide at 140°, crystallises from alcohol in white leaflets, melting at 191—192°; the *anilide*,

$$NHPh \cdot CH{:}CAc \cdot COOEt,$$

forms bright yellow, lustrous plates, and melts at 45—46°.

Methylic amidomethyleneacetoacetate crystallises from benzene in needles, and melts at 109°. The *anilide* and *paratoluidide* melt at 84—85°, and 86—87°, respectively.

Ethylic methenylbisacetoacetate, $COOEt \cdot CAc{:}CH \cdot CHAc \cdot COOEt$, is prepared by heating ethylic acetoacetate (2 mols.), ethylic orthoformate (1 mol.), and acetic anhydride (3 mols.), in a reflux apparatus for half a day (*loc. cit.*), or more conveniently, by the action of ethylic ethoxymethyleneacetoacetate on alcoholic ethylic sodioacetoacetate at the ordinary temperature. It crystallises from petroleum or carbon bisulphide in aggregates of short prisms, and melts at 96°; ferric chloride develops a bluish-violet coloration with the alcoholic solution.

Methenylbisphenylmethylpyrazolone,

$$\begin{array}{l} N{=}CMe \\ | \\ NPh \cdot CO \end{array}\!\!>\!C{:}CH \cdot CH\!<\!\!\begin{array}{l} CMe{:}N \\ \qquad\;\;| \\ CO{-}NPh \end{array},$$

obtained from phenylmethylpyrazolone and ethylic orthoformate, crystallises from ethylic acetate in orange-yellow needles, and melts at 180—181°. It is probably identical with the compound obtained by Besthorn and Knorr from the sodium derivative of phenylmethylpyrazolone and chloroform.

Ethylic methenylbisacetoacetate yields ethylic 2 : 6-dimethylpyridine-3 : 5-dicarboxylate when heated with ammonium acetate and glacial acetic acid in a reflux apparatus. Alcoholic sodium ethoxide converts the salt into *monethylic metahydroxyuvitate*,

$$COOEt \cdot C_6H_2Me(OH) \cdot COOH;$$

the *sodium* salt contains $3H_2O$, and melts and decomposes at 230—231°, the *silver* salt is anhydrous, and the *barium* salt contains $4H_2O$. The identity of the acid is established by hydrolysis, which converts it into metahydroxyuvitic acid, and by conversion into the *diethylic* salt of metahydroxyuvitic acid, which crystallises from petroleum in colourless plates melting at 50—51°; moreover, elimination of carbonic anhydride under the influence of heat converts the monethylic salt into *ethylic homoparahydroxybenzoate* [OH : Me : COOEt = 2 : 6 : 5], which melts at 92—93°, and boils at 306—308°.

Xanthophanic acid, $C_{18}H_{20}O_8$, is obtained by heating finely-powdered ethylic sodioacetoacetate (15·2 grams) with ethylic ethoxymethyleneacetoacetate (37·2 grams) in a reflux apparatus; it crystallises from alcohol in hemispherical aggregates of brownish-yellow needles, and melts at 143—144°. This compound is almost insoluble in water, but dissolves somewhat readily in cold benzene and glacial acetic acid, and very readily in chloroform; the alcoholic solution stains the skin intensely red, and develops a dark brownish-red coloration with ferric chloride. The solution in oil of vitriol is dark red, and exhibits beautiful fluorescence when heated. Ammonia, alkali carbonates, and a hot solution of potassium acetate dissolve the acid with production of a dark red coloration, and the solutions may be boiled without undergoing change, provided no caustic alkali is present. Xanthophanic acid is also formed when ethylic ethoxymethyleneacetoacetate is heated with potassium acetate and alcohol on the water bath. The *potassium*, *sodium*, and *barium* salts are red, crystalline substances, and dissolve readily in water. When boiled with excess of caustic soda, the sodium salt yields a colourless *compound*, $C_{15}H_{16}O_7$, which crystallises in short prisms, and melts at 118—120°; it is insoluble in water, but forms a golden-yellow solution in sodium carbonate, and the alcoholic solution develops a dark reddish-violet coloration with ferric chloride.

Glaucophanic acid, $C_{27}H_{26}O_{12}$, is a bye-product in the preparation of xanthophanic acid, forming about 10 per cent. of the product of the action of ethylic sodioacetoacetate on ethylic ethoxymethyleneacetoacetate; it crystallises from benzene in small, black needles with brownish-green reflex, and melts at 188—189°. It is scarcely soluble in cold water, but dissolves sparingly when the water is boiling, forming a dark blue solution; oil of vitriol also produces a dark blue solution. The *sodium* salt is very sparingly soluble in alcohol, from which it crystallises in small, green needles, with bronze reflex; the *ammonium* salt forms lustrous, greenish crystals.

Methoxymethyleneacetylacetone, $OMe{\cdot}CH{:}CAc_2$, is prepared by heating acetylacetone, acetic anhydride, and methylic orthoformate in a reflux apparatus for 40 minutes; it is a colourless oil which becomes red when kept, melts at 6—7°, and boils at 140° under a pressure of 16 mm.

When hydroxymethyleneacetylacetone (Abstr., 1894, i, 66), obtained by the action of water on ethoxymethyleneacetylacetone, is exposed to air, it gradually softens and becomes converted into an oil of penetrating and disagreeable odour, which liberates carbonic anhydride when heated; the alcoholic solution of hydroxymethyleneacetylacetone develops a dark, yellowish-red coloration with ferric chloride,

and the solution in oil of vitriol is pale yellow. Hydroxymethyleneacetylacetone is strongly acidic, and the solution in aqueous alcohol turns blue litmus red; the molecular conductivity in an infinitely dilute solution $\mu_\infty = 195$ at 2·6°. Hot caustic soda resolves it into formic aid and acetylacetone, and hot water alone produces the same effect after some time, a small portion of the substance becoming converted into triacetylbenzene. It is oxidised by mercuric oxide, yielding carbonic anhydride and acetylacetone. The *calcium* derivative contains $2H_2O$, but the *barium* and *silver* derivatives are anhydrous; the *mercurous* derivative is a yellowish-white, crystalline substance, becoming black spontaneously and depositing mercury; the *copper* derivative melts at 214°, the *ferric* derivative forms scarlet crystals melting at 124°, and the *ferrous* derivative brownish-yellow crystals. The *benzoyl* derivative of hydroxymethyleneacetylacetone crystallises from alcohol and melts at 71°; it becomes brown and soft when exposed to the air.

Amidomethyleneacetylacetone, $NH_2\cdot CH\colon CAc_2$, prepared by the action of alcoholic ammonia on ethoxymethyleneacetylacetone, crystallises from water in large, lustrous needles, melting at 144°; it gives no coloration with ferric chloride, but forms a crystalline, bluish-violet *copper* derivative, which dissolves in organic solvents and melts at 218°. The *acetyl* derivative crystallises from ethylic acetate in needles melting at 62°, and the *benzoyl* derivative also forms needles which melt at 101°; the *carbamide* derivative crystallises from alcohol in white needles and prisms, and melts and evolves gas at 187°. The *anilide* of hydroxymethyleneacetylacetone, $NHPh\cdot CH\colon CAc_2$, crystallises from petroleum in long, colourless needles, and melts at 90—91°; the *paratoluidide* and *benzylanilide* melt at 139—140° and 106° respectively.

Methenylbisacetylacetone, $CAc_2\colon CH\cdot CHAc_2$, is prepared by heating ethoxymethyleneacetylacetone, dissolved in absolute alcohol, with the potassium derivative of acetylacetone; it crystallises from ethylic acetate in aggregates of short, colourless prisms, and melts at 117—118° to a dark red liquid (Abstr., 1894, i, 67). The alcoholic solution develops a dark red coloration with ferric chloride, and the aqueous solution has an intensely bitter taste; the solutions in dilute alkalis, and alkali carbonates are golden yellow.

When an aqueous solution of the potassium derivative of methenylbisacetylacetone is boiled in a reflux apparatus for 6—8 hours, it yields *diacetylmetacresol* [OH : Ac_2 = 3 : 4 : 6] which crystallises from dilute acetic acid in long, white, lustrous needles, melts at 112°, and boils at 310°; the alcoholic solution develops a reddish-violet coloration with ferric chloride, and is sufficiently acidic to redden blue litmus paper. Dilute aqueous alkalis dissolve the substance readily, and it is also soluble in alkali carbonates, forming colourless solutions; the *potassium* and *barium* derivatives are colourless, crystalline substances. Ammonia converts diacetylmetacresol into the *compound* $CAc{<}{\begin{smallmatrix}CMe{=}CH\\CH\cdot CHAc\end{smallmatrix}}{>}C\colon NH$, which crystallises from alcohol in long, slender prisms, decomposing and melting indefinitely at 235°, after softening and becoming brown at 226°; when carefully

heated, it sublimes in a woolly mass of needles. The substance is isomeric with 3 : 5-diacetyl-2 : 6-dimethylpyridine(m. p. 73—74°), which is produced by the action of aqueous ammonia on methenylbisacetylacetone; the solution in cold dilute sulphuric acid is colourless, and precipitates the unchanged substance when treated with ammonia, but if the liquid is heated previously to the treatment with alkali, diacetylmetacresol is regenerated.

With E. HASSE.—Ethylic ethoxymethylenemalonate (*loc. cit.*) is prepared by heating ethylic malonate and ethylic orthoformate with acetic anhydride and zinc chloride in a reflux apparatus. Aqueous ammonia converts it into *ethylic amidomethylenemalonate*, $NH_2 \cdot CH:C(COOEt)_2$, which crystallises from petroleum in colourless plates and short prisms, melting at 67°; it is therefore identical with ethylic amidoethylenedicarboxylate (Ruhemann and Morrell, Abstr., 1895, i, 20), *ethylic anilidomethylenemalonate* being identical with *ethylic anilidoethylenedicarboxylate* (*loc. cit.*).

Methylic methoxymethylenemalonate, $OMe \cdot CH:C(COOMe)_2$, crystallises from a mixture of ethylic acetate and petroleum in aggregates of needles; it melts at 46°, and boils at 167° under a pressure of 20 mm.

Ethylic hydroxymethylenemalonate, $OH \cdot CH:C(COOEt)_2$, is obtained by treating an ethereal solution of the ethoxy-compound with the calculated quantity of alcoholic potash; it is a colourless oil, which boils at 107—109° under a pressure of 12 mm., and at 217—219° at the ordinary pressure; it has a sp. gr. = 1·128 at 20°. The alcoholic solution reddens blue litmus, and develops a dark, orange-red coloration with ferric chloride. The *potassium* derivative crystallises in short prisms, the *barium* derivative in white plates, and the *silver* derivative is crystalline, rapidly yielding the metal; the *copper* derivative crystallises from dilute alcohol in pale green needles melting at 119° when hydrated, and becomes dark green after removal of $1H_2O$, melting at 138° in the anhydrous condition.

Ethylic isoxazolone-β-carboxylate, $\begin{matrix} N:CH \\ | \\ O \cdot CO \end{matrix}\!\!>CH \cdot COOEt$, is prepared by heating ethylic ethoxymethylenemalonate with an alcoholic solution of hydroxylamine during 2 hours on the water bath; it separates from alcohol in small, white needles, and when crystallised from water resembles benzoic acid. When heated slowly, it melts, decomposing completely at 160—165°, this change taking place at 183—185° when the temperature rises quickly; the *silver* derivative is white and crystalline, the *ethyl* derivative crystallises in white needles, and melts at 46°, and the *methyl* derivative forms white needles and prisms melting at 96—97°. The action of hydroxylamine on ethylic ethoxymethylenemalonate is comparable with the behaviour of this substance towards phenylhydrazine, which gives rise to ethylic 1 : 5 : 4-phenylpyrazolonecarboxylate (Abstr., 1895, i, 193).

Ethylic methenylbismalonate (*ethylic dicarboxyglutaconate*),

$$(COOEt)_2C:CH \cdot CH(COOEt)_2,$$

is obtained by treating an alcoholic solution of ethylic sodiomalonate with the calculated quantity of ethylic ethoxymethylenemalonate; it is the intermediate production of this substance which accounts for

the residue of ethylic ethoxycoumalindicarboxylate obtained on distilling ethylic ethoxymethylenemalonate. Ruhemann and Guthzeit, who first prepared ethylic dicarboxyglutaconate, considered it remarkable that alkaline agents should so easily resolve the substance into malonic and formic acids. In the author's opinion, this change is explained by the fact that condensation products of organic acids with aliphatic compounds are, in general, easily resolved into their components by alkalis; moreover, those substances which contain negative radicles attached to ethylenic carbon frequently undergo decomposition involving assimilation of water, followed by rupture of the carbon chain, as instanced by the resolution of mesitylic oxide into two molecular proportions of acetone.

A valuable summary of facts relating to the production of hydroxymethylene compounds forms the conclusion of the paper.

M. O. F.

β-Lactone of *as*-Dimethylmalic Acid. By ADOLF VON BAEYER and VICTOR VILLIGER (*Ber.*, 1897, **30**, 1954—1958).—The existence of β-lactones of saturated open carbon chains has long been a matter of speculation, it is now found, however, that if the *monobrom*-as-*dimethylsuccinic acid* which crystallises from hydrochloric acid and melts at 167° be treated with silver oxide, the β-lactone of dimethylmalic acid, $CO{<}{}^{CMe_2}_{-O-}{>}CH{\cdot}COOH$, is produced. When first formed, the lactone gives figures on analysis corresponding with dimethylmalic acid, but on drying in a vacuum it gradually loses $1H_2O$, and then agrees with the lactone formula. The dried substance melts at 45—47°, but readily takes up $1H_2O$, melting then at 54—55°; titration of the dried substance showed it to be monobasic in the cold, but dibasic when warm, and a molecular weight determination proved it to be in reality a lactone, and not a lactide.

The lactone does not give off carbonic anhydride on distillation, and is obtained unchanged on evaporating its aqueous solution on the water bath; in the presence of alkali, however, it is instantly converted into dimethylmalic acid melting at 129—131°. The lactone is not re-formed from the acid when the latter is heated. J. F. T.

***cis*- and *trans*- Isomerism of Lactones.** By ADOLF VON BAEYER and VICTOR VILLIGER (*Ber.*, 1897, **30**, 1958—1962).—The isomerism between the two lactonic acids of hydroxycamphoronic acid, which are obtained by the bromination of camphoronic acid, must be geometric, since camphoronic acid, according to Bredt's formula, can only yield one hydroxy-derivative; the lactonic acid of hydroxydimethyltricarballylic acid was therefore prepared, and it was found that this compound existed in both the *cis* and the *trans* forms, the free carboxyl group in the former being on the one side of the lactone ring, and in the latter on the other side. The cis-*lactonic acid of hydroxydimethyltricarballylic acid*, prepared by decomposing bromodimethyltricarballylic acid with water, crystallises from water in large, many-sided prisms, melting at 207°. The trans-*lactonic acid* is the chief product formed in the oxidation, by means of chromic acid, of the dioxyisocamphoronic acid obtained from brominated isocamphoronic acid by

treatment with baryta; it is somewhat less soluble in water than the *cis*-modification, and forms slender prisms melting at 211—212°; on heating the *cis*-lactonic acid for 15 hours at 150°, it is for the most part (90 per cent.) converted into the *trans*-modification, and on heating the *trans*-acid in a similar way, a small quantity of the *cis*-compound is always produced. J. F. T.

Some Derivatives of Ethylic Diacetylsuccinate and Dibenzoylsuccinate. By CARL PAAL and FRIEDR. HÄRTEL (*Ber.*, 1897, **30**, 1991—1998).—Ethylic diacetylfumarate (Just, Abstr., 1886, 141) forms, with phenylhydrazine, a compound, $C_{22}H_{22}N_4O_3$; this melts at 138°, and decomposes when heated further, but yields no pyrazole-blue. *Ethylic dibenzoylfumarate*, $C_2Bz_2(COOEt)_2$, is obtained by suspending the sodium derivative of ethylic dibenzoylsuccinate in ether and acting on it with iodine; it melts at 75°. Boiled in acetic acid solution with occasional addition of strong ammonia, it yields ethylic 2 : 5-diphenylpyrroline-3 : 4-dicarboxylate, melting at 150—151° (Knorr, this vol., i, 66); if it is heated in acetic acid solution, and aqueous ammonia is then added, a substance melting at 195° is obtained. When hydrolysed with alcoholic alkali, it yields, beside an oil, two crystalline acids, one of which melts at 157—158°, and is presumably *dibenzoylmalic acid*, COOH·CHBz·CBz(OH)·COOH.

Ethylic bis-benzoyloxycrotonate, $C_2(CMe{\cdot}OBz)_2(COOEt)_2$, is obtained by suspending ethylic sodiodiacetylsuccinate in ether and treating it with benzoic chloride; it melts at 101°, and is converted by concentrated sulphuric acid into benzoic anhydride and ethylic carbopyrotritarate, $O{<}\begin{array}{l}CMe{:}C{\cdot}COOEt\\ CMe{:}\overset{|}{C}{\cdot}COOEt\end{array}$, by alcoholic ammonia into benzamide and ethylic 2 : 5-dimethylpyrroline-3 : 4-dicarboxylate,

$$NH{<}\begin{array}{l}CMe{:}C{\cdot}COOEt\\ CMe{:}\overset{|}{C}{\cdot}COOEt\end{array},$$

and by phenylhydrazine into benzoylphenylhydrazine and bisphenylmethylpyrazolone $C_2H_2\left({<}\begin{array}{l}CO{-}NPh\\ CMe{:}\overset{|}{N}\end{array}\right)_2$.

Ethylic bis-acetoxyphenylacrylate, $C_2(CPh{\cdot}OAc)_2(COOEt)_2$, is obtained by suspending ethylic sodiodibenzoylsuccinate in ether and treating it with acetic anhydride; it melts at 106°. By using benzoic instead of acetic chloride, *ethylic bis-benzoyloxyphenylacrylate*, $C_2(CPh{\cdot}OBz)_2(COOEt)_2$ can be obtained; it melts at 204°. C. F. B.

Xanthine Bases from Uric Acid. By ERNST EDUARD SUNDVIK (*Zeit. physiol. Chem.*, 1897, **23**, 476—482).—Although the relationship between uric acid and xanthine bases is undoubted, the observation of Strecker's, that uric acid can be converted into hypoxanthine by the use of sodium amalgam, is not confirmed. By heating an alkaline solution of uric acid, however, with chloroform, there were found, in addition to humous products, a substance, the silver compound of which contains from 83—84 per cent. of silver; silver cyanamide contains 84. In later experiments, two other substances were obtained, one of which resembles xanthine, the other hypoxanthine, but the identity is not absolute. W. D. H.

Nitrobarbituric and Nitrodimethylbarbituric Acids. By ARNOLD F. HOLLEMAN (*Rec. Trav. Chim.*, 1897, **16**, 162—171).—Nitrobarbituric and nitrodimethylbarbituric acids are nitroaliphatic compounds in which the *iso*-form is the stable one. The author has shown that several isonitro-compounds have an intense yellow colour in aqueous solutions; this appears to be always the case where the grouping $\begin{matrix}=\mathrm{C}\\ |\\ \mathrm{O}\end{matrix}\!\!>\mathrm{N{\cdot}OH}$ is combined with a sufficiently negative radicle.

Hantzsch and Schultze (Abstr., 1896, i, 353, 672) have demonstrated that aqueous solutions of real nitro-compounds have no electric conductivity, whereas a solution of an isonitro-compound conducts the electric current.

Nitrodimethylbarbituric acid is intensely yellow in aqueous solution, and this is caused by the anions; because on adding concentrated hydrochloric acid, which should considerably diminish ionisation, the colour almost entirely disappears. The molecular conductivity of this acid for one gram-molecule dissolved in v litres of water is 313·3 where $v = 32$ and 337·6 where $v = 1024$ (according to Ostwald, μ_∞ should be 352) so that in both dilutions the acid is almost completely ionised, a fact which renders it highly improbable that hydrogen is linked to that carbon atom which has the nitro-group attached to it.

Nitrobarbituric acid in aqueous solution is faintly coloured and has a molecular conductivity 323·4 where $v = 32$, and 341·4 where $v = 512$ (μ_∞ should be 356). Three hydrogen atoms in this acid are replaceable by metals, and when one equivalent of a base is added to its aqueous solution, the colour is not more altered than by adding an equal quantity of water; but the addition of a second equivalent of a base renders the solution intensely yellow. This may be explained by supposing that ionisation of the free acid takes place in such a way that one atom of hydrogen combined with nitrogen becomes the cathion whilst the anion complex (I) $\begin{array}{l}\mathrm{N{-\!\!-\!\!-}CO{-\!\!-\!\!-}NH}\\ |\qquad\qquad\qquad\quad |\\ \mathrm{CO{\cdot}C(NO_2)H{\cdot}CO}\end{array}$ is itself slowly ionised into H and (II) $\begin{array}{l}\mathrm{-N{-\!\!-}CO{-\!\!-}NH}\\ \;\;|\qquad\qquad\;\, |\\ \;\mathrm{CO{\cdot}CNO_2{\cdot}CO}\end{array}$.

This second anion is therefore the cause of the yellow colour; because, as the solution is almost completely ionised, the addition of a first equivalent of a base does not change the colour, for the reason that anion I is present after this addition; but the second equivalent causes almost the entire dissociation of anion I into anion II, and so the colour becomes intense.

The author has been unable to verify von Baeyer's statement that the barium salt of nitrobarbituric acid is not decomposed by sulphuric acid but only by sulphates; on the contrary, precipitation takes place just as well with free sulphuric acid as with potassium sulphate, and from consideration of ionisation, it could not be otherwise.

A. W. C.

Malonyldiethylcarbamide and 1 : 3-Diethyluric Acid. By KURT SEMBRITZKI (*Ber.*, 1897, **30**, 1814—1824).—When diethylcarbamide (11·2 grams) and malonic acid (6·2 grams) are warmed together

on the water bath in the presence of phosphorus oxychloride (6 grams) *malonyldiethylcarbamide* (*diethylbarbituric acid*), $CO<\begin{smallmatrix}NEt\cdot CO\\NEt\cdot CO\end{smallmatrix}>CH_2$, is formed; the crude syrupy product, weighing 40 per cent. of the theoretical yield, can be used for the subsequent syntheses. (If the three substances are heated in the proportions of 1 mol. of each, *acetylmalonyldiethylcarbamide*, $C_8H_{11}AcN_2O_3$, melting at 62·5°, is formed.) The pure substance crystallises in rhombic prisms and melts at 52—53°. When shaken with aqueous potassium or sodium nitrite, it forms salts of *diethylvioluric acid*, $CO<\begin{smallmatrix}NEt\cdot CO\\NEt\cdot CO\end{smallmatrix}>C:NOH + H_2O$, which itself melts at about 90°, or when anhydrous at about 107°. The *sodium* salt, $C_8H_{10}N_3O_4Na,C_8H_{11}N_3O_4 + 2H_2O$, is brick red; the *potassium* and *ammonium* salts are yellow, and have a similar composition; in the presence of excess of ammonia, a bluish-violet, anhydrous, normal ammonium salt is formed, but this yields the first-mentioned salt when it is recrystallised from water. The barium and lead salts are insoluble, the bluish-black ferrous salt slightly soluble, its solution having a characteristic deep blue colour. It affords a good test for diethylbarbituric acid, one part of which in 10,000 of water can be detected by adding a drop of sodium nitrite and ferrous sulphate, when a blue coloration is produced. When diethylvioluric acid is reduced with hydriodic acid, 1 : 3-*diethyluramil*, $CO<\begin{smallmatrix}NEt\cdot CO\\NEt\cdot CO\end{smallmatrix}>CHNH_2$, is formed; this reddens when heated, and melts and decomposes at about 200°. A good way of effecting the reduction is to dilute commercial hydriodic acid, of sp. gr. 1·96, with $\frac{1}{5}$th of its weight of water, cool 10 parts of this diluted acid to $-20°$, add 1 part of diethylvioluric acid gradually, shaking meanwhile, and then powdered phosphonium iodide, and continue the shaking, allowing the mixture gradually to attain the ordinary temperature. By heating diethyluramil (1 mol.) in the water bath with potassium cyanate ($1\frac{1}{2}$ mol.) in concentrated aqueous solution, 1 : 3-*diethyl-ψ-uric acid*, $CO<\begin{smallmatrix}NEt\cdot CO\\NEt\cdot CO\end{smallmatrix}>CH\cdot NH\cdot CO\cdot NH_2$, is obtained; it melts and decomposes at 196°, and when heated at 100°, with 25 per cent. hydrochloric acid in a flask with reflux condenser, yields 1 : 3-*diethyluric acid*, $\begin{smallmatrix}NEt\cdot CO\cdot C\cdot NH\\ | \qquad\quad \| \\ CO\cdot NEt\cdot C\cdot NH\end{smallmatrix}>CO$, which decomposes gradually when heated above 300°.

Malonyldiethylcarbamide yields *dibromomalonyldiethylcarbamide*,

$$CO<\begin{smallmatrix}NEt\cdot CO\\NEt\cdot CO\end{smallmatrix}>CBr_2,$$

when it is suspended in water and treated with bromine, and the same product is obtained from diethylvioluric acid; the new compound crystallises in monoclinic prisms [$a : b : c = 1·0284 : 1 : 2·3351$; $\beta = 85°$ $35\frac{1}{2}'$], and melts at 86—87° (corr.). An analogous *chloro*-derivative can be obtained by treating malonyldiethylcarbamide with a little water and strong hydrochloric acid, and adding potassium chlorate gradually; it melts at 87·5° (corr.). When malonyldiethylcarbamide is treated with strong nitric acid, and a drop of fuming nitric acid or a

trace of a nitrite added, a part of the product is insoluble in water and cold alcohol, but soluble in hot acetone, is colourless, melts and decomposes at 180° (corr.), and has the composition, $C_{16}H_{20}N_6O_9$. Another product, diethylalloxan, remains dissolved in the water; if this solution is treated with hydrogen sulphide and filtered from sulphur, it deposits colourless crystals of *tetrethylalloxantin*,

$$C_2(OH)_2\left(\begin{matrix}CO\cdot NEt\\CO\cdot NEt\end{matrix}\!\!>CO\right)_2,$$

which melts and decomposes at 162°, and can be reconverted into diethylalloxan by cautious oxidation with nitric acid. C. F. B.

Action of Alkaline Hypobromite on Asparagine. By W. van Dam (*Rec. Trav. Chim.*, 1897, **16**, 26—32).—According to present views, inactive and active asparagine have the following formulæ, respectively: I. $COOH\cdot CH_2\cdot CH(NH_2)\cdot CO\cdot NH_2$, II. $COOH\cdot CH(NH_2)\cdot CH_2\cdot CO\cdot NH_2$; and therefore, under the influence of alkaline hypobromite, reaction should take place according to the following equations:

I. $COOH\cdot CH(NH_2)\cdot CH_2\cdot CONH_2 + KOBr + 3KOH =$
$COOK\cdot CH(NH_2)\cdot CH_2\cdot NH_2 + K_2CO_3 + KBr + 3H_2O$

(with intermediate production of a bromamide).

II. $COOH\cdot CH_2\cdot CH(NH_2)\cdot CONH_2 + KOBr + 3KOH =$
$COOK\cdot CH_2\cdot CH(NH_2)_2 + K_2CO_3 + KBr + 3H_2O$.

The author has failed to substantiate the above theoretical views, for when natural asparagine is acted on by potassium hypobromite, although the yellow colour of the solution disappears, which would indicate the formation of a bromamide, the latter could not be isolated.

By varying the procedure so as to obtain any $\alpha\beta$-diamidopropionic acid which might have been formed, only the hydrochloride or hydrobromide of aspartic acid was obtained.

Apparently, alkaline hypobromite acts in this case as an oxidising agent, with production of carbonic and oxalic acids; nitrogen being recovered as ammonia.

If excess of hypobromite be used, bromoform is produced, together with the above-mentioned substances. A. W. C.

A New Asparagine. By Giovanni Sani (*Rend. Accad. Linc.*, 1895, **4**, ii, 214—217).—On heating a mixture of diethylic fumarate and benzylamine with alcohol at 130—135° in a closed tube for 48 hours, a *substance* of the composition

$$C_7H_7\cdot NH\cdot CO\cdot CH_2\cdot CH(NH\cdot C_7H_7)\cdot CO\cdot NH\cdot C_7H_7$$

is obtained; it crystallises in white flakes melting at 149—150°. On boiling with baryta solution, it gives benzylamine and the crystalline barium *salt* of *dibenzylasparagine*,

$$C_7H_7\cdot NH\cdot CO\cdot CH(NH\cdot C_7H_7)\cdot CH_2\cdot COOH$$

the acid crystallises in scales melting at 204—205°. W. J. P.

Acetodiphosphorous Acid. By Hans von Baeyer and Karl A. Hofmann (*Ber.*, 1897, **30**, 1973—1978).—When acetic acid (100 grams) is allowed to remain for 24 hours with phosphorus trichloride (80 grams), the mixture then heated for 1 hour in a reflux apparatus, and finally, after the chloride has been distilled off, for a few minutes at 120—130°, after which the residue is made alkaline with 7 per cent.

aqueous ammonia, ammonium chloride added, and then calcium chloride until the precipitate which forms at first has just disappeared, and the whole heated at 60—70°, *calcium diammonium acetodiphosphite*,

$$C_2P_2O_7H_4Ca(NH_4)_2,$$

eventually separates. If this salt is digested with aqueous silver nitrate, a *calcium silver* salt, $C_2P_2O_6H_3CaAg$, is formed; when it is warmed with aqueous hydroxylamine hydrochloride in the presence of a little alkali, a *calcium dihydroxylamine* salt, $C_2P_2O_7H_4Ca(NH_3OH)_2$, is formed, or a *calcium hydroxylamine* salt, $C_2P_2O_7H_5Ca(NH_3OH)$, if the hydroxylamine is present in great excess. A *manganese ammonium* salt, $C_2P_2O_7H_4Mn(NH_4)_2$, analogous to the calcium ammonium salt, can also be prepared. Further, if the crude product of the reaction described above is half neutralised with sodium carbonate, and ammonium chloride then added in amount rather more than equivalent to the sodium, a *disodium triammonium* salt, $C_2P_2O_7H_3Na_2(NH_4)_3$, is obtained, which contains H_2O after drying in a vacuum over sulphuric acid, and $6H_2O$ when dried over caustic potash in an atmosphere of ammonia. This salt loses $2NH_3$ at 110°, and, with silver nitrate, the residue yields a *silver* salt, $C_2P_2O_7H_5Ag_3$; if its solution is saturated with carbonic anhydride, a *disodium diammonium* salt, $C_2P_2O_7H_4Na_2(NH_4)_2 + 2H_2O$, separates; this loses NH_3 at 110°, and when crystallised from acid solutions yields a *sodium ammonium* salt, $C_2P_2O_7H_6Na(NH_4)$; if it is boiled for a long time with aqueous sodium hydroxide, the very soluble *sodium* salt, $C_2P_2O_7H_3Na_5 + 3H_2O$, separates: a potassium salt analogous to this was also prepared.

These salts are remarkably stable. They do not reduce mercuric, silver, or gold solutions, and they are not decomposed by boiling with nitric acid, aqua regia, or molybdate solution. Fuming nitric acid at 200° does decompose them, however, and so, in great part, does 15 per cent. sulphuric acid at 170°; some phosphoric acid and aldehyde are formed in the latter case. They are oxidised when boiled with aqueous potassium permanganate in the presence of dilute sulphuric acid, some manganese dioxide separating; 1 atom of oxygen is used up for each atom of phosphorus. These reactions are best explained by assigning the formula $OH\cdot CMe[PO(OH)_2]_2$ to the acid; its formation is probably preceded by that of acetylphosphorous acid, $CMeO\cdot PO(OH)_2$, (Menschutkin, *Annalen*, 1865, **133**, 317). C. F. B.

Dithienylethane, Dithienylethylene, and the Condensation of Thiophen with Benzotrichloride and Aluminium Chloride. By ALEXANDER NAHKE (*Ber.*, 1897, **30**, 2041—2043).—Phosphoric anhydride (75 grams) is gradually added to a mixture of thiophen (60 grams), monochloracetal (54 grams), chloroform (120 grams) and ether (30 grams), the whole is then warmed for a short time on the water bath and a further quantity (some 40 grams) of phosphoric anhydride is gradually added. After treatment with cold water, the mixture is extracted with chloroform, and the residue left on distilling off the chloroform is purified by distillation in steam at 130—140°. *Dithienylchlorethane* is thus obtained as a yellow oil distilling at 200—205° under a pressure of 25 mm. The same compound may be obtained by

the action of phosphoric anhydride on a mixture of thiophen and dichlorether. *Dithienylethylene,* which is formed when the above compound is repeatedly distilled at atmospheric pressure, crystallises from light petroleum in yellowish needles, melting at 125°. *Dithienylethylenic dibromide* melts and decomposes at 128°. *Dithienylbromethane* is a yellow, somewhat fluorescent oil, which distils at 200—210° under 30 mm. pressure, but, at the same time, undergoes partial decomposition. *Dithienyldichlorethane,* obtained from dichloracetal and thiophen, is a colourless oil distilling at 190—195° under 18 mm. pressure; on standing, it solidifies to glistening prisms melting at 32°. When treated with five times its weight of alcoholic potash (12 per cent.), it is converted into *dithienylchlorethylene,* which distils at 170—180° under 23 mm. pressure.

Benzotrichloride and thiophen yield dithienylphenylmethane, and not trithienylphenylmethane. J. J. S.

α-Dithienylethyl Methyl Ketone or Acetyl-α-dithienylethane. By ALEXANDER NAHKE (*Ber.*, 1897, **30**, 2040).—Phosphoric anhydride is added in small portions at a time to a solution of diacetyl (1 molecule) and thiophen (2 molecules) in chloroform, the anhydride being added until a fresh addition causes no further ebullition. After warming for some time on the water bath, water is added, the mixture extracted with ether, and the residue left after removal of the ether is subjected to steam distillation at 150—180°; the oil which passes over with the water, after being extracted with ether, and dried over calcium chloride, is obtained as a lemon-yellow oil boiling at 315—320°. The *hydrazone* is also an oil. J. J. S.

Dithienylphenylmethane—Its Nitro-, Amido-, and Sulphonic Derivatives. By ALEXANDER NAHKE (*Ber.*, 1897, **30**, 2033—2037. Compare Abstr., 1896, i, 690).—Better yields of dithienylphenylmethane, as well as of its three mononitro-derivatives, are obtained when the crude products are purified by distillation with superheated steam, instead of by extraction with dilute alcohol. By this method, 8 grams of dithienylphenylmethane can be obtained from 20 grams of thiophen.

Barium dithienylphenylmethanetrisulphonate,

$$[CH(C_4H_2S\cdot SO_3)_2\cdot C_6H_4\cdot SO_3]_2Ba_3 + 8H_2O.$$

—One to two grams of finely powdered dithienylphenylmethane is intimately mixed with sand which has previously been ignited and washed, and the mixture added to fuming sulphuric acid cooled with ice; the solution is then immediately poured into ice-cold water. When the mixture has been neutralised with barium carbonate, filtered, and the filtrate evaporated, the barium salt is obtained as an amorphous powder containing $8H_2O$; it is readily soluble in water, but practically insoluble in absolute alcohol. The *calcium* salt also contains $8H_2O$. Different salts of the nitro-sulphonic acids have also been prepared.

Dithienylmetamidophenylmethane is obtained as the *stannochloride* by reducing an alcoholic solution of the corresponding nitro-derivative with tin and concentrated hydrochloric acid; this double salt crystallises in needles, and decomposes at 210—220°. The free *base,* which

is best obtained by decomposing the above compound with sodium acetate solution, crystallises from light petroleum in needles melting at 73—74°, and dissolving readily in benzene, chloroform, or hot alcohol. The *hydrochloride* also crystallises in colourless needles, which turn red on exposure to the air and decompose at 225—235°. The *platinochloride* crystallises in yellow plates, and the *acetyl* derivative of the base in colourless plates melting at 115°.

Dithienylparamidophenylmethane crystallises in colourless needles melting at 84—85°, and its *hydrochloride* melts at 205—215°. The *acetyl* derivative crystallises in colourless plates, and melts at 142—143°.

Dithienylorthoamidophenylmethane is best obtained by reducing an alcoholic solution of the nitro-derivative with zinc dust and acetic acid. It crystallises in colourless needles melting at 59—60°, yields a *hydrochloride* and a sparingly soluble *nitrate*, a *platinochloride*, and an *acetyl* derivative melting at 153—154°. The *barium* salts of the three amidotrisulphonic acids are amorphous powders which readily char when heated. J. J. S.

Condensation of Iodothiophen with Benzaldehyde and of Thiophen with different Aldehydes. By ALEXANDER NAHKE (*Ber.*, 1897, **30**, 2037—2039).—Phosphoric anhydride (25 grams) is added to a mixture of iodothiophen (15 grams), benzaldehyde (8 grams), and chloroform (15 grams), and the whole heated on the water bath for 15—30 minutes. When cold, the phosphoric anhydride is hydrolysed with water, and the mixture extracted with chloroform; the residue left after distilling off the chloroform is dissolved in ether, any dark tarry matter is thrown down by vigorously shaking with light petroleum, and the residue from the ethereal solution, after being freed from iodothiophen and benzaldehyde by steam distillation, is crystallised from a mixture of alcohol and ether. The product, *di-iododithienylphenylmethane*, forms small, colourless needles melting at 89°.

Trithienylmethane, obtained by the action of phosphoric anhydride on an ethereal solution of thiophen and thiophenaldehyde, crystallises from light petroleum in colourless needles melting at 49—50°, and is readily soluble in benzene, ether, and hot alcohol. *Dithienylmetatolylmethane* may be obtained in a similar manner from thiophen and metatolualdehyde. It is a pale yellow oil boiling at 210—220° under a pressure of 20 mm. *Dithienylethane*, obtained from thiophen and paraldehyde, is a yellowish oil boiling between 270° and 280°; its odour somewhat resembles that of diphenylmethane. *Dithienylpropane* could not be obtained pure. *Dithienylheptane* is a yellow oil which distils at 200—203° under diminished pressure. J. J. S.

Synthesis of Cyclic Compounds by means of Ethylic Oxalate. By WILHELM WISLICENUS and AUGUST SCHWANHÄUSSER (*Annalen*, 1897, **297**, 98—113).—The formation of ethylic ketipate from ethylic acetate and ethylic oxalate suggested the possibility of producing cyclic systems by the agency of the latter salt. Experiment has now shown that this operation can be successfully performed only in the case of rings containing five carbon atoms; for instance, whilst ethylic oxalate and ethylic tricarballylate yield ethylic diketopenta-

methylenetricarboxylate, the salt has no ring-forming action on ethylic succinate or ethylic adipate (compare Wislicenus and Boeckler, Abstr., 1895, i, 506).

Ethylic 1 : 2-*diketopentamethylene*-3 : 4 : 5-*tricarboxylate*,

$$\begin{matrix} CO\cdot CH(COOEt) \\ | \\ CO\cdot CH(COOEt) \end{matrix}\!\!>\!CH\cdot COOEt,$$

is obtained from ethylic oxalate and ethylic propane-$\alpha\alpha_1\beta\beta$-tetracarboxylate (isoallylenetetracarboxylate) under the influence of sodium ethoxide (3 mols.); it crystallises from alcohol in colourless, lustrous prisms, and melts at 122—123°. The salt is insoluble in water, but dissolves readily in alkalis, alkali carbonates, and acetates; the alcoholic solution gives a dark red coloration with ferric chloride. It becomes completely charred when heated, without yielding carbonic oxide, and it cannot be distilled, even under a pressure of 10—15 mm., without undergoing decomposition; the substance is very indifferent towards alkali, and when heated with it in a reflux apparatus becomes brown in part, the remainder being converted into the corresponding alkali derivative; this behaviour prohibits hydrolysis, which, moreover, cannot be effected by hot dilute sulphuric acid, this giving rise to a compound which melts and boils at the same temperatures as diketopentamethylene (Dieckmann, this vol., i, 462), but can scarcely be identical with the latter, as it gives an intense coloration with ferric chloride. If less than three molecular proportions of sodium ethoxide are employed in the preparation of ethylic diketopentamethylenetricarboxylate, the yield is reduced, and a certain amount of *ethylic oxalopropane*-$\alpha\alpha_1\beta\beta$-*tetracarboxylate* (*oxalisoallylenetetracarboxylate*), $COOEt\cdot CO\cdot CH(COOEt)\cdot C(COOEt)_2\cdot CH_2\cdot COOEt$, is formed; the latter has not been isolated in the purified state, but its identity is established by its conversion, when distilled, into ethylic propanepentacarboxylate, $CH(COOEt)_2\cdot C(COOEt)_2\cdot CH_2\cdot COOEt$, obtained by Bischoff and Emmert from ethylic sodiomalonate and ethylic chlorethanetricarboxylate. Moreover, it develops a red coloration with ferric chloride, and yields ethylic diketopentamethylenetricarboxylate when acted on with sodium ethoxide in excess.

Although, in practice, the employment of ethylic propanetetracarboxylate for the preparation of ethylic diketopentamethylenetricarboxylate is more convenient, the substance is also produced by the action of sodium ethoxide (2 mols.) on a mixture of ethylic oxalate and ethylic tricarballylate. The *disodium* derivative of ethylic diketopentamethylenetricarboxylate forms colourless crystals, containing $3\frac{1}{2}H_2O$, which is lost at 120—130°; the *barium* derivative contains $1\frac{1}{2}H_2O$. The *osazone* crystallises from alcohol in yellow needles, and melts at 163—164°; treatment with a warm solution of ferric chloride produces a deep purple red colouring matter which dissolves in ether. The *tolazine*, $C_{21}H_{24}N_2O_6$, obtained by the action of orthotolylenediamine, crystallises in small needles, and melts at 141—142°.

Ethylic oxaladipate, $COOEt\cdot CO\cdot CH(COOEt)\cdot CH_2\cdot CH_2\cdot CH_2\cdot COOEt$, obtained by the action of sodium ethoxide on ethylic oxalate and ethylic adipate, is a colourless oil which develops an intense red coloration with ferric chloride. On attempting to distil it under

reduced pressure, carbonic oxide is eliminated, and *ethylic adipocarboxylate*, $COOEt\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH(COOEt)_2$, is produced. This is an oil which boils at 192—193° under a pressure of 26 mm., and does not give any coloration with ferric chloride. *Adipocarboxylic acid* melts at 139—140°, when it loses carbonic anhydride, and yields adipic acid.

M. O. F.

Hydrogenised Aromatic Compounds. By EMIL KNOEVENAGEL (*Annalen*, 1897, **297**, 113—137. Compare following abstracts and Abstr., 1896, i, 210).—Further investigation of the synthetical alkyl derivatives of hydrogenised toluene, obtained by reducing certain cycloid ketones (Abstr., 1896, i, 286), has shown that the compounds previously described as tetrahydrophenols or cyclohexenols (*loc. cit.*) are in reality hexahydro-derivatives or cyclohexanols, contaminated with a small proportion of less highly hydrogenised phenols. The fact was revealed on attempting to prepare cyclohexanols by the addition of hydrogen iodide to the supposed cyclohexenols, and submitting the products to reduction with zinc dust and glacial acetic acid. The phenols obtained in this way resembled so closely the original compounds as to suggest identity with them. Careful examination of the substances from this point of view has shown that reduction of the cyclohexenones with sodium and alcohol does actually give rise to the hexahydrophenols, thus emphasising the important fact that saturation of the third ethylenic linking of the benzene ring does not present the difficulty at one time associated with the operation; the experiments may, in fact, be regarded as lending support to Wagner's opinion that one ethylenic group in the carvone molecule is situated in the side chain.

Although, however, the supposed tetrahydrophenols are really hexahydrophenols, and, on oxidation with chromic acid yield hexahydroketones identical with those obtained on oxidising the corresponding hexahydrophenols of known character, the author recognises two series of stereoisomeric hexahydrophenols. Until fresh light is thrown on the question, the hexahydrophenols obtained by reducing cyclohexenones with sodium and alcohol will be referred to as *trans*-cyclohexanols, those obtained from the *trans*-cyclohexanols by treatment with hydrogen iodide, glacial acetic acid, and zinc dust being designated as *cis*-cyclohexanols.

The hydrocarbons obtained from the supposed tetrahydrophenols by the action of phosphoric anhydride must be henceforth regarded as tetrahydro-derivatives of benzene instead of dihydro-compounds.

M. O. F.

Constitution of Cyclohexenones obtained from 1:5-Diketones. By EMIL KNOEVENAGEL and A. SCHÜRENBERG (*Annalen*, 1897, **297**, 138—149. Compare Abstr., 1896, i, 210 and 286).—The constitutional formula, $CH{<}{\substack{CMe\cdot CH_2\\ CO—CH_2}}{>}CHR$, for the cyclohexenones obtained from 1:5-diketones (*loc. cit.*), is based upon their agreement in behaviour with typical ketones, the nature of their products of oxidation, and the relative position of the carbonyl and alkylic groups in the substances employed for their synthesis; the refractive constants,

however, uniformly agree more closely with those calculated for substances having the desmotropic enol-configuration,

$$CH{<}{}^{CMe-CH_2}_{C(OH):CH}{>}CHR.$$

In the case of 1-methylcyclohexenone-5, it is probable that the two forms are co-existent, because when the ketone is mixed with water, it is for the most part dissolved, but the undissolved residue is almost insoluble in water; if the soluble constituent is precipitated by potassium carbonate, and its physical properties compared with those of the insoluble portion, the molecular refraction of the former agrees with the calculated value for the enolic form, whilst the latter evidently has ketonic structure. The soluble constituent boils at 199—200°, has a sp. gr. = 0·9726 at 18·5°, and the refractive index $n_D = 1·4920$ at 18·5°, whence the molecular refraction R = 32·73; the insoluble portion boils at 200—201°, has a sp. gr. = 0·9624 at 20·5°, and the refractive index $n_D = 1·4711$ at 20·5°, whence the molecular refraction R = 31·88. The calculated constants for alcohol and ketone are 32·95 and 32·02 respectively.

The *oxime* of 1-methyl-3-isopropylcyclohexenone-5 occurs in two forms, one of which is obtained when the ketone is left in contact with an alkaline solution of hydroxylamine for several days at the ordinary temperature; it crystallises from alcohol, and melts at 88°. The second modification is prepared by treating the ketone with hydroxylamine hydrochloride (2 mols.), and adding a concentrated solution of caustic potash to the cooled liquid until it is feebly alkaline; after many days, water and dilute acetic acid are added, and the product extracted with ether. The oxime crystallises in plates, and melts at 117—118°; the *benzoyl* derivative melts at 155°.

The *phenylhydrazone* of 1-methyl-3-isopropylcyclohexenone-5 forms lustrous, sulphur-yellow crystals, which melt and decompose at about 60°; it becomes darker in the desiccator, and subsequently softens and decomposes.

In attempting to establish the alcoholic character of the cyclohexenones by means of the phenylcarbimide test, it has been shown that it may be applied to tertiary alcohols. The *phenylurethane* of trimethylcarbinol crystallises from ether and melts at 136°. The *phenylurethane* of metamethyldihydroresorcinol crystallises from benzene and melts at 96—97°; the action of heat resolves it into methyldihydroresorcinol and carbanilide. M. O. F.

Stages in the Hydrogenation of Toluene. By EMIL KNOEVENAGEL and J. TÜBBEN (*Annalen*, 1897, **297**, 150—160. Compare Knoevenagel, preceding page; also Abstr., 1896, i, 287 and 310).—cis-1-*Methylcyclohexanol*-5 (*hexahydrometacresol*) is obtained by treating with hydriodic acid dissolved in glacial acetic acid the alcohol formerly described as tetrahydrometacresol, now recognised as hexahydrometacresol contaminated with a small proportion of the tetrahydro-derivative; after 12 hours, the product is reduced with zinc dust, and gently heated on the water bath, the metallic powder being added until iodine is removed from the compound. At this stage, the product contains a large proportion of acetyl derivative, and is therefore

hydrolysed with aqueous barium hydroxide; after removal of oxidisable impurities and treatment with sodium hydrogen sulphite, it boils at 174—175° (corr.) under a pressure of 760 mm., sp. gr. = 0·91905 at 16°, and the refractive index $n_D = 1·4579$ at 16°, whence the molecular refraction R = 33·77; it is less viscous than the *trans*-modification, is readily volatile in steam, and resembles menthol in odour and taste. The substance is indifferent towards bromine or dilute solutions of potassium permanganate. The *acetyl* derivative has an agreeable, fruity odour, and boils at 193—194° under a pressure of 754 mm.; the *phenylurethane* crystallises from alcohol, and melts at 91°.

5-*Chloro*-1-*methylcyclohexane* is prepared by heating the alcohol with concentrated hydrochloric acid in sealed tubes at 100°; it is a colourless oil of sp. gr. 0·9706 at 15°/4°, and boils at 56—57° under a pressure of 10 mm. 5-*Bromo*-1-*methylcyclohexane* is a colourless, oily liquid, gradually becoming brown when exposed to light; it has a sp. gr. = 1·2543 at 15°/4°, and boils at 70—71° under a pressure of 10 mm. 5 : 1-*Iodomethylcyclohexane* is colourless, but becomes brown under the influence of light; its sp. gr. = 1·5516 at 15°/4°, and it boils at 82—83° under a pressure of 10 mm. (compare Wallach, Abstr., 1896, i, 310).

1-Methylcyclohexanone-5 is prepared by agitating *cis*-methylcyclohexanol with a slight excess of Beckmann's chromic acid mixture; it boils at 169—170° under a pressure of 760 mm., has a sp. gr. = 0·9213 at 19·3°/4°, and the refractive index $n_D = 1·44174$, whence the molecular refraction R = 32·10. It is a colourless, mobile liquid, having the taste and odour of peppermint, and is indifferent towards bromine and potassium permanganate solutions. 1-Methylcyclohexanone-5 has also been obtained by Wallach from pulegone and formic acid (Abstr., 1896, i, 309), by Tiemann and Schmidt from the oxime and semicarbazone of isopulegone (Abstr., 1896, i, 383), by the same authors from isopulegone and formic acid (this vol., i, 198), and by Einhorn and Ehret from the distillation of β-methylpimelic acid with sodalime (this vol., i, 345), whilst Zelinsky and Generosoff have described an isomeride which they obtained from α-methylpimelic acid (Abstr., 1896, i, 350); the constants recorded by the various authors are tabulated in the paper.

Methylcyclohexene (tetrahydrotoluene) is the substance previously described as dihydrotoluene (Abstr., 1896, i, 288); it boils at 105—106° under a pressure of 760 mm., has a sp. gr. = 0·8048 at 20·3°/4°, and the refractive index $n_D = 1·4454$, whence the molecular refraction R = 31·70 (compare Wallach, Abstr., 1896, i, 310). The *dibromide* is a colourless liquid which becomes green, and subsequently darkens spontaneously; it boils at 117—118° under a pressure of 117—118 mm., and has a sp. gr. = 1·5718 at 15°/4°.

Methylcyclohexane (hexahydrotoluene), prepared by reducing the iodide of cyclohexanol with zinc dust and glacial acetic acid, boils at 103° under a pressure of 760 mm., has a sp. gr. = 0·7662 at 18·5°/4°, and the refractive index $n_D = 1·41705$, whence the molecular refraction R = 32·09. The hydrocarbon is a mobile liquid having the odour of petroleum, and is indifferent towards solutions of bromine and potassium permanganate (compare Zelinsky and Generosoff, Abstr., 1896, i, 351).

M. O. F.

Stages in the Hydrogenation of Metaxylene. By EMIL KNOEVENAGEL and MACGARVEY (*Annalen*, 1897, **297**, 160—168. Compare foregoing abstract).—cis-1 : 3-*Dimethylcyclohexanol*-5 (*hexahydro*-1 : 3 : 5-*xylenol*) is prepared from the substance previously described as tetrahydro-1 : 3 : 5-xylenol (Abstr., 1896, i, 287) by the action of hydriodic acid, followed by treatment with zinc dust and glacial acetic acid ; it is less viscous than the *trans*-modification (the tetrahydro-derivative in question), and has an agreeable odour suggesting that of menthol. It boils at 187—187·5° under a pressure of 760 mm., has a sp. gr. = 0·9109 at 21°/4°, and the refractive index n_D = 1·4540, whence the molecular refraction R = 38·01. The *acetyl*-derivative, which is a mobile liquid having the odour of amylic acetate, boils at 201—202° under a pressure of 748 mm., has a sp. gr. = 0·9226 at 21°/4°, and the refractive index n_D = 1·4370, whence the molecular refraction R = 48·21. The *phenylurethane* crystallises from a mixture of alcohol and petroleum, and melts at 110°. 1 : 3-*Dimethylcyclohexanylic*-5 *bromide* boils at 67—69° under a pressure of 6 mm., and at 185—190° under the ordinary pressure, when it undergoes partial decomposition ; it has a sp. gr. = 1·2037 at 15°/4° ; the *iodide*, which has a sp. gr. = 1·4390 at 15°/4°, boils at 92—93° under a pressure of 10 mm., but decomposes when distilled under the ordinary pressure.

1 : 3-*Dimethylcyclohexanone*-5, produced on oxidising *cis*-dimethylcyclohexanol with Beckmann's chromic acid mixture, is a colourless oil, insoluble in water, having the odour of menthol, and is indifferent towards solutions of bromine and potassium permanganate. It boils at 181—182° under a pressure of 760 mm., has a sp. gr. = 0·8994 at 17°/4°, and the refractive index n_D = 1·4450, whence the molecular refraction R = 37·31 ; an isomeride has been prepared by Zelinsky (Abstr., 1895, i, 339), by Noyes (Abstr., 1896, i, 696), and by Kipping (Trans., 1895, 349). The *semicarbazone* crystallises from benzene and melts at 190—191°, whilst the *semicarbazone* of 1 : 3-dimethylcyclohexenone-5 (Abstr., 1895, i, 52) melts at 179—180° ; the *oxime* melts at 73°.

Δ^5-1 : 3-*Dimethylcyclohexene* (tetrahydrometaxylene) is the compound previously described as dihydrometaxylene (Abstr., 1896, i, 288) ; it boils at 124—125° under a pressure of 760 mm., has a sp. gr. = 0·8005 at 18°/4°. and the refractive index n_D = 1·443, whence the molecular refraction R = 36·43. The *dibromide* is a yellow oil which becomes greenish when kept ; it boils at 105—107° under a pressure of 6 mm., and has a sp. gr. = 1·5390 at 18·5°/4°.

1 : 3-*Dimethylcyclohexane* (hexahydrometaxylene) is prepared by reducing the iodide of 1 : 3-cyclohexane-5. It boils at 120° under a pressure of 760 mm., has a sp. gr. = 0·7736 at 18°/4°, and the refractive index n_D = 1·4270, whence the molecular refraction R = 37·06 ; it is identical with Zelinsky's 1 : 3-dimethylhexamethylene (Abstr., 1895, i, 339). A hot mixture of nitric and sulphuric acids converts the hydrocarbons into trinitrometaxylene. M. O. F.

Symmetrical Menthol. By EMIL KNOEVENAGEL and G. WIEDERMANN (*Annalen*, 1897, **297**, 169—174).—cis-1 : 3-*Methylisopropylcyclohexanol*-5 (cis-*symmetrical menthol*) is obtained by the action of

hydriodic acid, zinc dust, and glacial acetic acid on the substance previously described as tetrahydro-1 : 3 : 5-carvacrol (Abstr., 1896, i, 287), but consisting really of *trans*-hexahydro-1 : 3 : 5-carvacrol contaminated with a small quantity of less highly hydrogenised alcohol (compare Knoevenagel, this vol., i, 606). It is less viscous than the isomeride, boils at 226—227° under a pressure of 760 mm., has a sp. gr. = 0·9020 at 13·6°/4°, and the refractive index $n_D = 1·46454$ at 13·6°, whence the molecular refraction R = 47·67. It has an agreeable odour suggesting menthol, and is indifferent towards potassium permanganate and bromine. The *acetyl*-derivative boils at 235—236° under a pressure of 752 mm. ; the *phenylurethane* crystallises from a mixture of petroleum and alcohol, and melts at 88°. The *chloride* boils at 94—96° under a pressure of 12 mm., decomposing when distilled under atmospheric pressure ; it has a sp. gr. = 0·9720 at 14°/4°. The *bromide* has a sp. gr. = 1·1992 at 15°/4°, and boils at 104—106° under a pressure of 12 mm. ; the *iodide* has a sp. gr. = 1·4016 at 16°/4°, and boils at 133—134° under a pressure of 12 mm.

1 : 3-Methylisopropylcylohexanone-5 (*sym*-menthone) is prepared by oxidising *cis*-methylisopropylcyclohexanol with Beckmann's chromic acid mixture ; it is a colourless, limpid oil, having a feeble odour of peppermint, and readily forms a crystalline compound with sodium hydrogen sulphite. It boils at 222° under a pressure of 749 mm., has a sp. gr. = 0·9040 at 18°/4°, and the refractive index $n_D = 1·45359$ at 18°, whence the molecular refraction R = 45·98. The *semicarbazone* crystallises from benzene and melts at 176—177°. The *semicarbazone* of 1 : 3-methyl*iso*propylcyclohexenone-5 melts at 166—167°.

1 : 3-*Methylisopropylcyclohexene* (*meta-menthene*), prepared by heating *cis*-symmetrical menthol with phosphoric anhydride at 110—130°, is a colourless, limpid liquid, having the odour of petroleum when freshly distilled, but more closely resembling turpentine after being kept. It decolorises a cold, dilute solution of potassium permanganate and a solution of bromine in chloroform. The substance boils at 169—170° under a pressure of 746 mm., has a sp. gr. = 0·8197 at 16°/4°, and the refractive index $n_D = 1·45609$, whence the molecular refraction R = 45·67. The *dibromide* decomposes when distilled under atmospheric pressure, and boils at 153—155° under a pressure of 19 mm. ; it has a sp. gr. = 1·5210 at 16°/4°.

1 : 3-*Methylisopropylcyclohexane* (*meta-menthane*) is obtained by reducing the iodide of symmetrical menthol ; it boils at 167—168° under a pressure of 756 mm., has a sp. gr. = 0·8033 at 14°/4°, and the refractive index $n_D = 1·44204$, whence the molecular refraction R = 46·02. It is indifferent towards concentrated sulphuric and nitric acids, and also to solutions of potassium permanganate and bromine. M. O. F.

Corrections regarding Tetrahydrophenols and Dihydrobenzenes. By EMIL KNOEVENAGEL and K. WEDEMEYER (*Annalen*, 1897, 297, 175—185).—This paper contains the experimental evidence on which is based Knoevenagel's conclusion that the substances previously described as tetrahydrophenols (Abstr., 1896, i, 287) must be now recognised as hexahydro-derivatives. Particulars are given which relate to the conversion of *cis*- and *trans*-cyclohexanols into cyclohexa-

nones, and it is shown that under the influence of sodium and boiling alcohol *trans*-cyclohexanols are regenerated, thus affording a method of passing from the *cis*- to the *trans*-modification; *trans*-cyclohexanols are converted by phosphoric anhydride into the tetrahydro-derivatives of the corresponding hydrocarbons. M. O. F.

Synthesis and Constitution of Isophorone. By EMIL KNOEVENAGEL and C. FISCHER (*Annalen*, 1897, **297**, 185—203).—1 : 3 : 3-*Trimethylcyclohexenone*-5 (isophorone), $CMe\lessdot\begin{matrix}CH_2\cdot CMe_2\\ CH\text{——}CO\end{matrix}\gtrdot CH_2$, is prepared by treating mesitylic oxide and ethylic acetoacetate with alcoholic sodium ethoxide at the ordinary temperature; after 8 days the liquid is heated on the water bath for 4 hours, hydrolysed with 20 per cent. sulphuric acid, and submitted to distillation in a current of steam. It is identical with the compound described by Fittig (*Annalen*, 1859, **110**, 23), and subsequently by Kerp (Abstr., 1896, i, 447). It boils at 213—214° under a pressure of 760 mm.; it has a sp. gr. = 0·9228 at 18°/4°, and the refractive index $n_D = 1·4766$ at 18°, whence the molecular refraction R = 42·22. As in the case of all other cyclohexenones derived from 1 : 5-diketones, therefore, the optical properties are in closer agreement with the enolic formula (R = 42·16) than with the ketonic configuration (R = 41·22); from a chemical point of view, however, isophorone behaves exclusively as a ketone. It has an agreeable odour of peppermint, and a penetrating, cooling taste; it decolorises solutions of potassium permanganate and bromine immediately in the cold. The *semicarbazone* crystallises in slender, white needles, and melts at 186°; the phenylhydrazone melts at 68—69°. The oxime boils at 134° and 153° under pressures of 16 mm. and 40 mm. respectively, and melts at 74—75° (compare Kerp, *loc. cit.*); the *benzoyl* derivative crystallises in white needles and melts at 99°.

5 : 1 : 3 : 3-*Chlorotrimethylcyclohexadiene* is obtained by adding phosphorus pentachloride to a solution of isophorone in chloroform; it boils at 62° under a pressure of 12 mm., and rapidly becomes brown.

5 : 1 : 3 : 3-*Amidotrimethylcyclohexene* (*isophorylamine*), the base obtained by Kerp on reducing the oxime with sodium and alcohol, boils at 77° under a pressure of 16 mm., and the *hydrochloride* and *benzoyl* derivatives melt at 200° and 122° respectively.

trans-*Dihydroisophorol* (trimethylcyclohexanol) is prepared by reducing isophorone with sodium and alcohol; after distillation, and crystallisation from ether, it melts at 34·5°, and boils at 95° under a pressure of 15 mm., and at 196° under a pressure of 760 mm.; it has a sp. gr. = 0·8778 at 40°/4°. *cis*-Dihydroisophorol is produced when the crude *trans*-modification, which still contains less highly hydrogenised constituents, is treated with hydrogen iodide, and subsequently reduced with zinc dust and acetic acid; it boils at 92° and 201—203° under pressures of 12 mm. and 750 mm. respectively, has a sp. gr. = 0·8096 at 40°/4°, and the refractive index $n_D = 1·4550$, whence the molecular refraction R = 42·77. The *acetyl* derivative of both forms boils at 209—210°.

Dihydroisophorone is obtained by oxidising *cis*- and *trans*-dihydro-

isophorol with Beckmann's chromic acid mixture, and has the odour of peppermint; it boils at 189—190° under a pressure of 752 mm., has a sp. gr. = 0·8923 at 15°/4°, and the refractive index n_D = 1·4455, whence the molecular refraction R = 41·79. The ketone is indifferent towards solutions of bromine and potassium permanganate, and forms a crystalline *compound* with sodium hydrogen sulphite; the *oxime* and *semicarbazone* melt at 58° and 204° respectively.

1 : 3 : 3-*Trimethylcyclohexene*, is produced by the action of phosphoric anhydride on trimethylcyclohexanol, both modifications of which yield the same hydrocarbon; it is a limpid liquid having the odour of petroleum, boils at 139—141°, has a sp. gr. = 0·7981 at 23°/4°, and the refractive index n_D = 1·4453, whence the molecular refraction R = 41·35. The hydrocarbon immediately decolorises solutions of bromine and potassium permanganate; it is probably identical with isogeraniolene (Tiemann and Semmler, Abstr., 1894, i, 85).

The *iodide* of dihydroisophorol is obtained by heating *cis*-dihydro-isophorol with hydriodic acid in sealed tubes in the water bath; it is a pale yellow liquid, becoming brown when exposed to light, boils at 97—98° under a pressure of 12 mm., and has a sp. gr. = 1·3804 at 20°/4°.

1 : 3 : 3-*Trimethylcyclohexane* is prepared by reducing the iodide with zinc dust and glacial acetic acid; it boils at 137—138° under a pressure of 760 mm., has a sp. gr. = 0·7848 at 15°/4°, and the refractive index n_D = 1·4324 at 15°, whence the molecular refraction R = 41·68.

M. O. F.

Derivatives of Cycloheptane. By EDUARD BUCHNER (*Ber.*, 1897, **30**, 1949—1950).—By the addition of hydrogen cyanide to suberone and hydrolysis of the product formed, a neutral compound is obtained melting at 130°, and evidently *hydroxycycloheptacarbonamide*,

$$OH\cdot C_7H_{12}\cdot CO\cdot NH_2,$$

which on boiling with hydrochloric acid yields the corresponding hydroxycycloheptanecarboxylic acid (suberylglycollic acid) melting at 79—80°.

J. F. T.

Hexahydrobenzophenone and its Oximes. By VICTOR MEYER and W. SCHARVIN (*Ber.*, 1897, **30**, 1940—1943).—It was formerly held that oximes containing a fatty and an aromatic group, attached to the carbon atom of the oxime residue, do not exist in two forms because the mobility of the less massive aliphatic radicle enabled the isomerism to escape detection. This is controverted by Claus, in view of the fact that stearophenone, in which the fatty radicle far outweighs the aromatic, yields but one oxime (this vol., i, 187), and an explanation has been put forward by this investigator based on a transformation peculiar to aromatic radicles and becoming apparent when two such groups are present. The authors, however, have observed isomerism in the case of hexahydrobenzophenone, a substance containing only one of those groups in which the rearrangement indicated by Claus could take place. Consequently, the fact that ketoximes containing fatty radicles do not exhibit isomerism remains without explanation.

Hexahydrobenzoic *chloride* boils at 179°, and has a penetrating odour resembling that of benzoic chloride.

Hexahydrobenzophenone, $C_6H_{11}\cdot COPh$, is obtained by treating hexahydrobenzoic chloride with benzene and aluminium chloride; it crystallises from ether and from light petroleum in colourless needles and melts at 54°. The *α-oxime*, obtained from the product by the action of hydroxylamine on the ketone by fractional precipitation with water from its solution in acetic acid, crystallises from alcohol in slender, lustrous needles, and melts at 158°; the *β-oxime*, which is more readily soluble, crystallises in short prisms, and melts at 111°.

Octanoylbenzene (*phenyl heptyl ketone*), $C_7H_{15}\cdot COPh$, is obtained from octoic chloride, benzene, and aluminium chloride; it crystallises in colourless needles, melts at 22°, and boils at 164° under a pressure of 44 mm. The *oxime* crystallises in needles, and melts at 50°; it does not exhibit isomerism.

M. O. F.

Condensation of Phloroglucinol with Sugars and Aldehydes.

By CONSTANTIN COUNCLER (*Chem. Zeit.*, 1896, **20**, 585—586 and 599).—The condensation product of phloroglucinol and *d*-fructose, previously described (Abstr., 1895, i, 164), is more readily obtained when hydrogen chloride is passed into a mixture of 6 parts of *d*-fructose and 5·4 parts of phloroglucinol suspended in 15 parts of hydrochloric acid (sp. gr. = 1·124). In order to determine, if possible, the constitution of fructosephloroglucide, $C_{36}H_{34}O_{17}$, the author has subjected it to the action of chlorine and bromine. Bromine water acts on a dilute alcoholic solution of the compound, yielding a *bromo*-derivative, $C_{36}Br_{11}H_{23}O_{17}$, which is unstable. A *chloro*-derivative, $C_{36}Cl_{13}H_{21}O_{17}$, can be obtained in a similar manner, and is somewhat more stable; it can only be freed from the last traces of water with great difficulty. Fructosephloroglucide, when kept for some time, loses water and yields the *anhydride*, $C_{72}H_{66}O_{33}$, which is also amorphous and decomposes without melting.

Sorbinose phloroglucide can be obtained as a gelatinous mass, which on drying loses water and yields the *anhydride*, $C_{72}H_{62}O_{31}$. Phloroglucinol also reacts with Lintner's β-hydroxy-δ-methylfurfuraldehyde (Abstr., 1896, i, 144), yielding a condensation product, $C_{24}H_{18}O_9$ or $C_{48}H_{38}O_{19}$.

Phloroglucinol forms condensation products with fatty aldehydes much more readily than with sugars. When phloroglucinol (1 mol.) and the aldehyde (1 mol.) are brought into contact with an excess of hydrochloric acid (12 per cent.), a copious amorphous precipitate is formed. *Formaldehydephloroglucide*, $C_{13}H_{12}O_6$, is best obtained by working in methyl alcoholic solution; it is insoluble in water, but dissolves in alcohol yielding a yellow solution, and begins to decompose at 155°. *Acetaldehydephloroglucide*, $C_{22}H_{22}O_9$, is a golden-yellow precipitate which melts and decomposes at 216°. *Propaldehydephloroglucide*, $C_{33}H_{36}O_{12}$, begins to sinter at 153°. *Isobutyraldehydephloroglucide*, $C_{26}H_{30}O_9$, is a pale rose coloured precipitate melting at 166°. None of the products could be obtained in a crystalline form. They all appear to be formed according to the general equation:

$$mC_nH_{2n}O + (m+1)C_6H_6O_3 = mH_2O + C_{6+m(n+2)}H_{6+2m(n+6)}O_{3(m+1)}$$

J. J. S.

Isomeric Amidines. By REINHOLD WALTHER (*J. pr. Chem.*, 1897, **55**, [ii], 552).—The author as yet sees no reason to doubt the existence of isomeric phenyltolylmethenylamidines (Wheeler, this vol. i, 465). A further paper on the subject will be published.

C. F. B.

β-Substituted Hydroxylamines. By CARL KJELLIN (*Ber.*, 1897, **30**, 1891—1895).—*Isopropylmetanitroisobenzaldoxime*,

$$\begin{array}{l} NO_2\cdot C_6H_4\cdot CH \\ \quad CHMe_2\cdot N \end{array}\!\!>\!O,$$

is obtained by the action of isopropylic bromide or iodide on metanitrobenz*syn*aldoxime. It crystallises from benzene in small, yellow prisms melting at 138°, is sparingly soluble in ether, but readily in alcohol or hot benzene, and its ethereal solution gives a white precipitate with hydrogen chloride.

β-Isopropylhydroxylamine hydrochloride, $CHMe_2\cdot NH\cdot OH,HCl$, obtained when the above compound is hydrolysed with concentrated hydrochloric acid, crystallises in large prisms melting at about 55°. The free *base* obtained by treating the hydrochloride with a little less than the theoretical quantity of sodium dissolved in methylic alcohol sublimes in long, silky needles melting at 87°. It is easily soluble in water or alcohol, but only sparingly in benzene or ether. It readily absorbs moisture, reduces Fehling's solution, and is decomposed when strongly heated.

Hydroxyisopropylcarbamide, $NH_2\cdot CO\cdot NPr^{\beta}\cdot OH$, crystallises from water or alcohol in broad needles, melts and decomposes at 104—106°, is insoluble in ether, and gives a reddish-blue coloration with ferric chloride.

Propylmetanitroisobenzaldoxime crystallises in small needles, melts at 65°, and is extremely soluble in alcohol or ether. *Propylhydroxylamine hydrochloride* is an oil, and the free *base* crystallises in white needles melting at 46°; the latter is readily soluble in the usual solvents with the exception of light petroleum.

Hydroxypropylallylthiocarbamide, $C_3H_5\cdot NH\cdot CS\cdot NPr\cdot OH$, crystallises in needles and melts at 53—54°; with ferric chloride, it gives a greenish-blue coloration.

The author has also repeated his work on the action of concentrated hydrochloric acid on β-alkylhydroxylamines (Abstr., 1894, i, 10). In each case, 1—2 grams of the hydroxylamine was heated with three times its weight of concentrated hydrochloric acid for 3 hours at 210—220°. β-Methylhydroxylamine gave ammonia together with a minute quantity of methylamine; β-ethylhydroxylamine gave no ethylamine; β-benzylhydroxylamine gave ammonia and benzoic acid but no benzylamine; orthonitrobenzylhydroxylamine yielded ammonia as the only base. With β-isopropylhydroxylamine, ammonia and mesityl oxide were obtained but no isopropylamine; the mesityl oxide was doubtless formed by the condensation of the acetone liberated in accordance with the following equation

$$CHMe_2\cdot NHOH = COMe_2 + NH_3.$$

J. J. S.

A New Method of Formation of Bisnitrosylbenzyl. By CARL KJELLIN and K. G. KUYLENSTJERNA (*Ber.*, 1897, 30, 1896—1900. Compare Behrend, Abstr., 1891, 1032; 1892, 1199).—When chlorine is passed into a well-cooled aqueous solution of β-benzylhydroxylamine or of its hydrochloride, a greenish, flocculent precipitate is obtained, which, after being washed with water and dried, becomes a white powder melting at 73°. It contains chlorine, and when kept for some time is transformed into a dark coloured oil. When boiled with hydrochloric acid, it yields hydroxylamine, whilst heating with methylic alcohol gives rise to benzaldoxime and bisnitrosylbenzyl melting at 128—129°; a better yield of the latter may be obtained by gradually adding bromine water to a solution of β-benzylhydroxylamine in 50 parts of water. Bisnitrosylparanitrobenzyl may be prepared in a similar manner.

Parabromobenzylisobenzaldoxime, $O<\begin{array}{l}CHPh\\ \mid\\ N\cdot CH_2\cdot C_6H_4Br\end{array}$, is formed together with the oxygen ether when *syn*benzaldoxime is alkylated in the usual manner with parabromobenzylic bromide; after recrystallisation from hot alcohol, it melts at 128°. When boiled with 15 times its weight of concentrated hydrochloric acid until all drops of oil have disappeared, it yields *parabromobenzylhydroxylamine hydrochloride* melting and decomposing at 188°. The free *base* is insoluble in water, but is readily soluble in methylic alcohol or hot benzene; it crystallises in small needles melting at about 85°. *Bisnitrosylparabromobenzyl*, $(C_6H_4Br\cdot CH_2\cdot NO)_2$, obtained together with an equal quantity of parabromobenzaldoxime by the action of bromine water on the hydroxylamine, crystallises from hot chloroform in beautiful, short prisms, which melt and decompose at 137—138°. When boiled with alcohol, it is decomposed into the oxime, but it is only slowly hydrolysed by alkalis or by acids. When finely divided and allowed to stand for several days with a 10 per cent. solution of sodium hydroxide, it yields a mixture of *parabromobenz*-syn-*aldoxime* and *parabromobenz*-anti-*aldoxime*; a solution of sodium in methylic alcohol acts much more readily. On passing carbonic anhydride through the diluted alkaline solution the *syn*-aldoxime is first precipitated and then the *anti*-compound can be obtained; whereas if the solution is neutralised with a mineral acid, the *anti*-oxime alone is obtained. The *syn*-aldoxime, which is most readily obtained by intramolecular transformation from the *anti*-compound, crystallises in broad, glistening needles melting at 157°, and is readily soluble in alcohol, benzene, or ether. The *anti*-aldoxime crystallises from light petroleum in colourless needles melting at 108°.

Bisnitrosylorthonitrobenzyl is a white powder melting at 141°; it is more readily acted on by sodium hydroxide than the isomeric parabromo-derivative. An alcoholic solution of sodium ethoxide gives a yellow solution which on treatment with the requisite quantity of methylic iodide yields Goldschmidt and Rietschoten's ethers $O<\begin{array}{l}NMe\\ \mid\\ CH\cdot C_6H_4NO_2\end{array}$ and $\begin{array}{l}NO_2\cdot C_6H_4\cdot CH\\ \qquad\qquad\quad \Vert\\ \qquad\quad MeON\end{array}$ (Abstr., 1893, i, 709).

J. J. S.

Action of Bromine on β-Benzylhydroxylamine and the Constitution of the Bisnitrosylbenzyls. By CARL KJELLIN (*Ber.*, 1897, **30**, 1969—1971).—The equation $(x+y)R\cdot CH_2\cdot NH\cdot OH + (x+y)Br_2 = xRCH\colon N\cdot OH + \frac{y}{2}(R\cdot CH_2\cdot NO)_2 + 2(x+y)HBr$ is an exact representation of the action which occurs when a benzylhydroxylamine hydrochloride is treated with bromine, and the author considers that Behrend's formula for the bisnitrosyl compound produced, namely, $RCH_2\cdot N{<}{}^{O}_{O}{>}N\cdot CH_2R$, is the only one possible. J. F. T.

Action of Furfuraldehyde on Aromatic Hydroxylamines. By ROBERT ERHARDT (*Ber.*, 1897, **30**, 2016—2018).—Furfuraldehyde readily reacts with phenylhydroxylamine in alkaline solution, forming *furfurylidenephenylazoxime*, $C_4OH_3\cdot CH{<}{}^{O}_{NPh}$, which crystallises in white, silky needles melting at 91—92°. It decomposes on exposure to light or when its aqueous solution is boiled for some time. *Furfurylideneorthotolylazoxime* crystallises in large, yellow tablets melting at 58°, and resembles the foregoing compound in its properties. No compound could be obtained with paratolylhydroxylamine.

A. H.

Isomeric Diazoamido-compounds. By REINHOLD WALTHER (*J. pr. Chem.*, 1897, [ii], **55**, 548—552).—The alternative formula proposed by the author for these compounds, is not $NH{<}{}^{NR}_{NR}$, as Hantzsch supposes (this vol., i, 468), but $NR\colon NH\colon NR$. Objections to it are discussed.

By extracting crude diazoamidobenzene, which melts at 98° or 100° when pure, with cold light petroleum, an isomeride is obtained which melts at 79—80°; if kept at this temperature for a few minutes, it solidifies, and then melts at 90—91°. Further, if dissolved in alcohol and reprecipitated with water, it then melts at 88—93°, and, after a repetition of this treatment, at 97—98°. Possibly this and the ordinary diazoamidobenzene may have the formulæ $NR\colon N\cdot NHR$ and $NR\colon NH\colon NR$. C. F. B.

Isomerism of Compounds from Diazonium Salts and Ethylic Acetoacetate. By CARL KJELLIN (*Ber.*, 1897, **30**, 1965—1969).—It has already been shown that the compounds formed by the condensation of diazonium chlorides with ethylic cyanacetate always exist in two isomeric forms, and it is now found that the same rule applies, although not to such a marked extent, to compounds derived from the condensation of diazonium chlorides with ethylic acetoacetate. The condensation product of *diazonium chloride* and *ethylic acetoacetate*, $N_2Ph\cdot CHAc\cdot COOEt$, melts at 80—84°, but on solidifying and remelting melts at 48—60°, and if boiled with alcohol for some time, at 43—50°; the two isomerides could not be separated. The product from *orthochlorodiazonium chloride* and *ethylic acetoacetate*,

$$C_6H_4Cl\cdot N_2\cdot CHAc\cdot COOEt,$$

melts at 80—83°, but on recrystallisation from alcohol the melting point falls to 59—61°; the isomeride of higher melting point is regenerated on treating it with alcoholic potash. With the compound from *para-chlorodiazonium chloride*, no isomerism was noticeable; the compound from ethylic *acetoacetate* and sym-*tribromodiazonium bromide*,

$$C_6H_2Br_3N_2\cdot CHAc\cdot COOEt,$$

forms yellow needles melting at 95—109° or 95—113°, which, on fractional recrystallisation from light petroleum, is separated into fractions melting at 121—123° and 117—121° respectively, each of which, on solidifying and remelting, melts at 95—109°.

In the following compounds, no isomerism could be detected.

Metachlorodiazobenzene ethylic acetoacetate, $C_6H_4Cl\cdot N_2\cdot CHAc\cdot COOEt$, which crystallises from light petroleum in dark yellow prisms melting at 70—80°.

Orthobromodiazobenzene ethylic acetoacetate, $C_6H_4Br\cdot N_2\cdot CHAc\cdot COOEt$, forming yellow needles melting at 65—70°.

Orthonitrodiazobenzene ethylic acetoacetate,

$$NO_2\cdot C_6H_4\cdot N_2\cdot CHAc\cdot COOEt,$$

consisting of glistening leaflets melting at 85—95°; the *para-nitro-*derivative crystallises from alcohol in yellow needles melting at 122—123° and the *orthochlorodiazobenzenenitroethane*,

$$C_6H_4Cl\cdot N_2\cdot CHMe\cdot NO_2,$$

in orange-yellow leaflets melting at 112° with decomposition.

J. F. T.

"Hypnoacetin" [Acetophenoneparacetamidophenol]. By G. Vignolo (*Rend. Accad. Linc.*, 1895, 4, i, 358—361).—The author has prepared, by a method which he will publish later, *acetophenoneparacetamidophenol*, $COPh\cdot CH_2\cdot O\cdot C_6H_4\cdot NHAc$; this crystallises in transparent laminæ of pearly lustre melting at 160° with decomposition. The name hypnoacetin is given to it on account of its hypnotic action.

W. J. P.

Iodosobenzoic Acids. By H. Kretzer (*Ber.*, 1897, 30, 1943—1948).—Diorthiodo-derivatives of benzoic acid, according to the law of etherification, should not yield ethylic salts when treated with alcohol and hydrogen chloride, and, further, should only take up one atom of oxygen on oxidation. Some difficulty was found in the preparation of diorthiodobenzoic acid itself, but the corresponding chlorotri-iodobenzoic acid was found to agree in every way with the above generalisations, and was prepared in the following way. Metamidobenzoic acid, on iodisation, yields *tri-iodamidobenzoic acid*,

$$[COOH : NH_2 : I_3 = 1 : 3 : 2 : 4 : 6],$$

which crystallises from dilute alcohol in colourless leaflets melting and decomposing at 196°; this, on diazotisation, reduction to the hydrazine, and oxidation with ferric chloride, gives 3 : 2 : 4 : 6-*chlorotri-iodobenzoic acid*, which crystallises in glistening plates melting at 226°, and does not yield an ethylic salt on treatment with alcohol and hydrogen chloride.

Chlorodi-iodoiodosobenzoic acid is prepared from chlorotri-iodobenzoic acid by oxidation with potassium permanganate in acid solution, the compound being separated by treating the product with sodium carbonate when the iodoso-acid remains undissolved; it is almost insoluble

in water and melts at 206°. The *acid dichloride*, produced on suspending the acid in chloroform and saturating with chlorine, is a yellow powder melting at 204° with evolution of gas; by prolonging the action of the chlorine, the *tetrachloride* is obtained melting at 206° with evolution of gas. J. F. T.

Phenylglycine and Phenylglycineorthocarboxylic Acid: and their Behaviour in the Animal Body. By JÖRGEN E. THESEN (*Zeit. physiol. Chem.*, 1897, **23**, 23—29).—On account of the ease with which phenylglycine and phenylglycineorthocarboxylic acid can be converted into indoxyl derivatives, experiments were made to ascertain if similar changes take plate in the organism, but without success. In the case of phenylglycine, which is very poisonous to dogs and rabbits, but apparently without toxic effect on frogs, no albumin or sugar appears in the urine. Jaffé's reaction is not more marked and the relative amount of ethylsulphuric acid is not increased. How phenylglycine is secreted could not be definitely proved on account of the very small doses which could be given to animals, and also on account of the few characteristic properties of this substance. With phenylglycineorthocarboxylic acid, which can be given to both dogs and rabbits in large doses without toxic symptoms, the same results were obtained, with the addition of the fact that the unchanged carboxylic acid could be easily detected in the urine.

Indoxylsulphuric acid is synthesised if the product of the fusion of phenylglycineorthocarboxylic acid with caustic potash is treated with potassium pyrosulphate; the residue is then repeatedly extracted with alcohol, and the alcoholic solution concentrated, when amidobenzoic acid separates out. The mother liquor contains the potassium salt of indoxylsulphuric acid, which crystallises from absolute alcohol in white, glistening crystals.

Dibenzylindoxyl, $C_8H_5NO(C_7H_7)_2$, obtained by the action of benzylic chloride on the product of the fusion of phenylglycineorthocarboxylic acid with potassium hydroxide, crystallises from dilute alcohol in yellow crystals melting at 166°. It is insoluble in water but easily soluble in alcohol and ether; its concentrated alcoholic solution is dark red, and the dilute solution has a beautiful green fluorescence. A. W. C.

Action of Alkaline Potassium Hypobromite on certain Amides. Preparation of Methenedioxyamidobenzene. By A. R. VAN LINGE (*Rec. Trav. Chim.*, 1897, **16**, 44—56. Compare Van Dam, this vol., i, 601).—Piperonylic acid is best prepared by oxidising piperonal with an alkaline solution of potassium hypobromite, when 99 per cent. of the theoretical yield is obtained. When similarly treated, benzaldehyde is converted into benzoic acid and phenanthraquinone into diphenic acid.

Ethylic piperonylate, obtained by saturating a solution of the free acid in alcohol with hydrogen chloride, is a yellow oil, which solidifies to a mass of crystals belonging to the orthorhombic system. It melts at 18·5°, boils at 285·5—286·5°, and is almost insoluble in water, but readily soluble in ether, alcohol, and light petroleum.

Jobst and Hesse have described this substance as an oil boiling between 170° and 200°.

Methylic piperonylate, obtained by a similar method, crystallises in monoclinic needles, melts at 51·5°, and boils at 273—274°.

Piperonylamide is obtained by heating a mixture of methylic piperonylate with aqueous ammonia in sealed tubes at 120°. From dilute alcohol, it crystallises in beautiful, rhombic crystals containing $1H_2O$, and from absolute alcohol in rhombohedral plates. It sublimes without decomposition, is soluble in alcohol and ether, and nearly insoluble in water and light petroleum. By the action of potassium hypobromite in the cold, it is converted into the corresponding *bromamide*; it forms small, white crystals, which readily decompose with evolution of hydrogen bromide.

Methenedioxyamidobenzene, prepared by heating together piperonylamide and an alkaline solution of potassium hypobromite, forms white needles melting at 44°; it is readily soluble in alcohol, ether, chloroform, and carbon tetrachloride, but only sparingly so in water or light petroleum. It decomposes on distillation under diminished pressure, and its aqueous solution, which turns brown on exposure to air, possesses strongly reducing properties, precipitating platinum and silver from solutions of their salts. With calcium hypochlorite, a dilute solution of the base gives a fugitive red, and, with ferric chloride, a dark, violet coloration. The *hydrochloride* is a yellow powder; the *hydrobromide* crystallises in woolly needles; the *nitrate* forms colourless, quadratic plates, decomposing on exposure to moist air and acquiring a red tint; the *sulphate* is obtained as long needles when a concentrated solution of the hydrochloride is treated with ammonium sulphate; the *oxalate* forms rhombic crystals which turn yellow under water; the *picrate* crystallises in yellow needles which decompose with violence when heated, and the *platinochloride* forms small needles, decomposing slowly in the air, and rapidly when heated. The *cadmiochloride* forms colourless crystals. The salts of the base are non-poisonous, and their solutions gradually acquire the property of fluorescing.

The author has studied the action of alkaline potassium hypobromite on the diamides of malonic, succinic, and fumaric acids, in the hope of obtaining amines of the composition $NH_2{\cdot}CH_2{\cdot}NH_2$, $NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$, and $NH_2{\cdot}C{:}C{\cdot}NH_2$, but without success, as oxidation takes place and the whole of the nitrogen is eliminated as ammonia.

When fumaric bromamide is treated with potassium hypobromite at − 2°, maleamide is formed.

A. W. C.

Action of Nitric Acid on the Methylamides of Phenylacetic and Phenylpropionic Acids. By H. J. Taverne (*Rec. Trav. Chim.*, 1897, **16**, 33—43.)—Van Romburgh (*Rec. Trav. Chim*, iv, 384) has shown that when the methyl derivatives of benzamide are treated with nitric acid, a nitro-group enters the combination in the nucleus.

Although the position of the nitro-group with regard to the methylamide group has not been determined, it seems probable, considering the result obtained with benzamide itself, that it would occupy the same positions as in the nitration of benzoic acid, namely, ortho and para.

The methylamides of benzoic acid, on treatment with nitric acid, do not behave like those of acetic acid, which are decomposed under these circumstances; the monomethylamide with production of the nitramide, and the dimethylamide giving nitrodimethylamine. If benzoic acid be looked on as phenylformic acid, and acetic acid as methylformic acid, the difference in the action of nitric acid on their methylamides may perhaps be attributed to the difference in the nature of the methyl and phenyl groups.

The question then arises whether the methylamides of phenylacetic acid compared with those of methylacetic (propionic) acid and also the methylamides of phenylpropionic acid compared with those of methylpropionic (butyric) acid, show the same difference in their behaviour with nitric acid; or, in other words, if the phenyl group, when at a greater distance from the methylamide group, still exercises the same influence. Already, in the nitration of the acids themselves, a difference has been noticed; for whilst benzoic acid gives ortho- and meta- (principally meta-) nitrobenzoic acids, phenylacetic and phenylpropionic acid yield ortho- and para-compounds, and principally the para-compound. As a result of his investigation, the author finds that the methylamides of phenylacetic and phenylpropionic acid react with nitric acid in the same way as those of phenylformic (benzoic) acid, the distance of the phenyl group from the amide group apparently exerting no influence. Although during the nitration of the acids themselves the ortho- and para-nitro-acids are formed, in the case of the methylamide the para-compounds alone are produced. It seems, therefore, that the amide group does exert a certain influence on the reaction.

Phenylacetomethylamide, $CH_2Ph\cdot CO\cdot NHMe$, prepared by the action of methylamine hydrochloride on phenylacetic chloride, is crystalline, melts at 58°, is slightly soluble in water and benzene, and easily soluble in alcohol, ether, and chloroform. By the action of nitric acid, a *nitromethylamide* melting at 156—157° is formed, and this contains the nitro-group in the nucleus, as is proved by treating it with concentrated hydrochloric acid, when paranitrophenylacetic acid is produced. Methylamine is obtained on treating the nitroamide with caustic potash.

Phenylacetodimethylamide, $CH_2Ph\cdot CO\cdot NMe_2$, prepared in a similar manner, is crystalline, melts at 43·5°, and boils at 155° under a pressure of 10 mm. It is easily soluble in ether, chloroform, benzene, and water; and when acted on with nitric acid is converted into a *nitrodimethylamide* melting at 90—91°; dimethylamine is produced when the latter is decomposed with caustic potash, whilst with concentrated hydrochloric acid paranitrophenylacetic acid is obtained.

Phenylpropionomethylamide, $CH_2Ph\cdot CH_2\cdot CO\cdot NHMe$, produced by the interaction of methylamine hydrochloride and phenylpropionic chloride, is crystalline and melts at 59—60°. The corresponding *nitromethylamide* separates from chloroform solution in silken needles melting at 166—167°; when treated with potash, this yields monomethylamine, and with hydrochloric acid, paranitrophenylpropionic acid.

Phenylpropionodimethylamide, $CH_2Ph\cdot CH_2\cdot CO\cdot NMe_2$, is a colourless, syrupy liquid boiling at 162° under a pressure of 10 mm. The *nitrodimethylamide* obtained from it by the action of nitric acid forms acicular crystals melting at 90—91°. With caustic potash, it yields

dimethylamine, and with hydrochloric acid, paranitrophenylpropionic acid. A. W. C.

Phthalimide. By JOHN A. MATHEWS (*J. Amer. Chem. Soc.*, 1896, **18**, 679—682).—By heating phthalic acid and propionitrile with a few drops of acetic anhydride in a sealed tube at 180—200°, the author has obtained a 92·5 per cent. yield of phthalimide. E. W. W.

Parachlorobenzonitrile. By L. VAN SCHERPENZEEL (*Rec. Trav. Chim.*, 1897, **16**, 113—115).—*Parachlorobenzonitrile* is prepared by diazotising parachloraniline, and adding the diazo-compound gradually to a solution of copper cyanide, maintaining the temperature at 90°. When the action is ended, the nitrile is distilled with steam.

It crystallises from alcohol in slender, white needles melting at 90°, (which is considerably higher than the melting point of either the ortho- or meta-compound), and boils without decomposition at 223° under a pressure of 750 mm. It is slightly soluble in water and easily so in alcohol, ether, and benzene.

The identity of the substance was proved by converting it into parachlorobenzoic acid, and also into the amide of this acid.

A. W. C.

Peroxides of the Acid Radicles. III. By LUDWIG VANINO (*Ber.*, 1897, **30**, 2003—2005. Compare Abstr., 1894, i, 416; 1896, i, 597).—Benzoic peroxide, which smells like bleaching powder, is not attacked by hydrochloric acid of sp. gr. = 1·19 at 120°, but is decomposed by it at a higher temperature with separation of carbon. Hydrofluoric acid is not affected by it, whilst hydrobromic and hydriodic acids are rapidly oxidised, as is also formaldehyde. The peroxide is only slowly attacked by zinc and hydrochloric acid and by sodium amalgam.

Nitrobenzoic peroxide, melting at 140—141°, can be obtained colourless by repeated crystallisation from alcohol; it is converted by alcoholic ammonia into ammonium nitrobenzoate and by phenylhydrazine into *phenylhydrazine nitrobenzoate*, which melts at 142—143°.

Phthalic peroxide does not appear to yield a nitro-product. None of the organic peroxides oxidise hydrochloric acid, and they are only very slowly acted on by potassium permanganate. A. H.

Benzophenone Derivatives. By PIETRO BARTOLOTTI (*Gazzetta*, 1897, **27**, ii, 18—25).—On heating pyrogallol trimethyl ether with zinc chloride and benzoic chloride at 100° without using a solvent, the principal product is benzoylpyrogallol dimethyl ether,

$$COPh\cdot C_6H_2(OMe)_2\cdot OH,$$

which crystallises in large, yellow prisms melting at 130—131°; a small proportion of benzoylpyrogallol dimethyl ether is formed simultaneously.

Acetylbenzoylpyrogallol dimethyl ether, $COPh\cdot C_6H_2(OMe)_2\cdot OAc$, prepared in the usual way, forms white crystals melting at 104—105°; the corresponding *benzoyl* derivative, obtained by Baumann's method, separates from ethylic acetate in white crystals melting at 111°.

Benzoylpyrogallol trimethyl ether, $COPh\cdot C_6H_2(OMe)_3$, [COPh : $(OMe)_3$ = 1 : 2 : 3 : 4 or 1 : 3 : 4 : 5], prepared by the action of methylic iodide and soda on benzoylpyrogallol dimethyl ether or of benzoic chloride and zinc

chloride in benzene solution on pyrogallol trimethyl ether, is a liquid of high boiling point; on determining the methoxyl in it by Zeisel's method, Graebe and Eichengrün's 1 : 2 : 3-trihydroxybenzophenone is obtained (Abstr., 1891, 706). W. J. P.

Action of Furfuraldehyde on Paradiamines. By ROBERT ERHARDT (*Ber.*, 1897, **30**, 2012—2016).—When tolidine is heated with furfuraldehyde at 100°, condensation occurs and a *difurfurylidene* compound, $C_4OH_3 \cdot CH{:}N \cdot C_6H_3Me \cdot C_6H_3Me \cdot N{:}CH \cdot C_4OH_3$, is formed, which crystallises in golden-yellow plates, melts at 188—189°, and is readily hydrolysed by heating with dilute acids. Benzidine reacts with furfuraldehyde in a similar manner, yielding a *compound* which crystallises in small, yellow needles melting at 231—232°; this does not appear to be the same as that described by Schiff (Abstr., 1878, 668), since it does not give a carmine red coloration when treated with dilute acid in alcoholic solution. The *compound* obtained from dianisidine forms small, yellow plates melting at 181—182°; like the benzidine compound, it gives with ferric chloride in alcoholic solution a reddish-brown coloration, whilst the tolidine compound gives a yellowish-brown, which becomes olive green on heating. Paraphenetidine also reacts with furfuraldehyde to form a *condensation product*, which is very unstable, but crystallises from ether in yellow tablets melting at 72—73°, and gives a blood-red coloration with ferric chloride in alcoholic solution. It readily unites with bromine and iodine, the compound with the latter element forming a splendid magenta coloured solution in alcohol. A. H.

Stereoisomerism of the Phenylnitrocinnamic Acids. By MARUSSIA BAKUNIN (*Gazzetta*, 1897, **27**, ii, 34—48).—The author has previously described (Abstr., 1895, i, 531) the *trans*-phenylnitrocinnamic acids and, from the mother liquors obtained in their preparation, has isolated the isomeric *cis*- or *allo*-compounds; he now gives further particulars respecting the isomerism of these acids.

Allo-phenylparanitrocinnamic acid melts at 143° and is not converted into the *trans*-isomeride melting at 214° by exposure to diffused light, boiling with iodine, or by adding iodine to the fused substance; the conversion is brought about, however, by several days' exposure to bright sunlight in alcoholic solution, either pure or in presence of iodine or carbon. The *allo*-ortho-acid melting at 147° was not converted into the *trans*-isomeride melting at 195° by iodine. The conversion of the *allo*-meta-acid melting at 195° into the *trans*-acid melting at 181° is hindered by the presence of iodine, but is brought about by exposure to bright sunlight and hastened by the presence of carbon; the incandescent gas light seems incapable of effecting the inter-conversions. The ortho- and para-*trans*-acids do not change into the *allo*-isomerides under the influence of sunlight, but the meta-*trans*-acid in alcoholic solution either alone or, better, in presence of carbon is partially converted into the *allo*-isomeride by direct sunlight.

The *trans*-acids do not combine with aniline, whereas the *allo*-isomerides combine readily with it, giving crystalline salts.

Aniline allophenylorthonitrocinnamate, $C_{15}H_{11}NO_4,NH_2Ph$, crystallises in yellow needles melting at 133°; the meta-*isomeride* crystallises in

yellow laminæ melting at 161—162° and the para-*isomeride* melts at 167—168°.

Paratoluidine allophenylorthonitrocinnamate, $C_{15}H_{11}NO_4,NH_2\cdot C_6H_4Me$, crystallises in yellow needles melting at 105°; the *salt* of the meta-acid forms yellow scales melting at 143—144° whilst the *salt* of the para-acid crystallises in yellow needles melting at 181—182°.

Barium allophenylmetanitrocinnamate separates from water in large, transparent crystals containing 4·5 H_2O or in aggregates of needles containing $3H_2O$. The *methylic* salt of the *allo*-meta-acid melts at 113—115° and that of the para-acid at 148·5°. The same *amido*-derivative $C_{15}H_{15}NO_2$, which melts at 199—200°, is obtained on reducing both the *allo*- and *trans*-para-acids with sodium amalgam.

W. J. P.

Stereoisomeric Phenylcinnamic Acids. By MARUSSIA BAKUNIN (*Gazzetta*, 1897, **27**, ii, 48—55).—The most convenient method of preparing the phenylcinnamic acids seems to be to heat together benzaldehyde (10 grams), sodium α-toluate (15 grams) and acetic anhydride (40 grams) at 180°, in an oil bath, for 6 hours; 75 per cent. of the yield is ordinary or *trans*-phenylcinnamic acid melting at 170—172° and the remaining 25 per cent. contains the isomeric *allo*-acid which melts at 136—137°. Stilbene is formed at the same time.

Allo-phenylcinnamic acid gives a *barium* salt which crystallises with $5H_2O$ and $3H_2O$, combines readily with aniline to form a normal salt melting at 128°, and yields a liquid *methylic* salt. The *barium* salt of the *trans*-acid crystallises with $4H_2O$, and the acid does not combine with aniline, but gives a solid *methylic* salt; the *allo*-acid is more soluble in water then the *trans*-acid.

W. J. P.

Dimethylic Ether of Dibromophenolphthalein. By ERNESTO GRANDE (*Gazzetta*, 1897, **27**, ii, 67—70).—By the interaction of orthobromanisol and phthalic chloride, in presence of aluminium chloride, the author has prepared the dibromo-derivative of the dimethylic ether of phenolphthalein which he previously obtained by brominating the ether (Abstr., 1896, i, 563). The dibromo-derivative therefore, contains two groups of the constitution $-C\lessgtr\begin{matrix}CH\cdot CBr\\CH:CH\end{matrix}\gtrdot C\cdot OMe$ and its constitution is fully determined.

The dibromo-derivative dissolves in 5 parts of water at 17°, and when treated with concentrated sulphuric acid gives a yellow crystalline compound which sublimes at 220—230°, contains bromine, and behaves like a hydroxyanthraquinone. When the dibromo-derivative is treated with concentrated hydriodic acid, it gives a mixture of compounds and does not wholly lose its methoxyl.

W. J. P.

Tetraphenylmethane. By MOSES GOMBERG (*Ber.*, 1897, **30**, 2043—2047).—*Triphenylmethane hydrazobenzene*, $CPh_3\cdot NH\cdot NHPh$, is obtained when phenylhydrazine (2 mols.) is added to an ethereal solution of triphenylbromomethane; the ethereal solution, after gently warming on the water bath, is filtered from the precipitate of phenylhydrazine hydrobromide, the filtrate evaporated, and the crystalline residue purified by recrystallisation from benzene or ether. It is a

feeble base combining, in ethereal solution, with hydrogen chloride, oxalic acid, picric acid, &c. The melting point is about 135°, but is not sharp, since the compound is readily oxidised to *triphenylmethaneazobenzene*, $CPh_3 \cdot N \colon NPh$. The latter is most conveniently obtained by suspending the finely divided hydrazo-compound in ether, and adding amylic nitrite and a few drops of acetic chloride, the yellow crystals which separate being recrystallised from alcohol or ether; the yield is good, and the melting point of the azo-compound is 111°. *Tetraphenylmethane* is obtained when the azo-compound is heated above its melting point, or when heated at a lower temperature with copper bronze ("kupferbronze") or platinum sponge.

It can also be obtained by heating a toluene or xylene solution of the azo-compound. The author recommends the following process: triphenylmethaneazobenzene (8 grams) is added in small portions to copper bronze (1 gram) heated at 110°, the molten mass being stirred from time to time; when the evolution of gas has ceased, the residue is extracted with hot benzene, filtered, and the residue left on distilling off the benzene is dissolved in a very little benzene and set aside for 2—3 days. The crystals thus obtained are washed with light petroleum, and then recrystallised several times from benzene. From 8 grams of the azo compound, only 0·3 gram of pure tetraphenylmethane melting at 267·5° (uncorr.) is obtained. The compound is insoluble in ether, acetic acid, or light petroleum, but is readily soluble in hot benzene. J. J. S.

Paradimethylethyloctahydronaphthalene. By AMERICO ANDREOCCI (*Rend. Accad. Linc.*, 1895, **4**, i, 431—435).—On boiling a mixture of santonin, hydrochloric acid, cupric chloride and tin for 10 hours on a sand bath, there is formed, in addition to santonous acid, a paradimethylethyloctahydronaphthalene, $C_{14}H_{24}$, which distils over on heating the liquid, and can be freed from chlorine by boiling with sodium; it boils at 247·4—247·8°, and gives the normal vapour density by V. Meyer's method when heated by diphenylamine vapour in an atmosphere of hydrogen. The crude hydrocarbon contains a little chlorine, owing, probably, to the presence of an additive compound with hydrogen chloride, $C_{14}H_{25}Cl$, which boils at a higher temperature than the hydrocarbon; the hydrocarbon has an odour of mint probably due to contamination with an oxygenated compound. W. J. P.

Puglia Olive Oil. By FRANCESCO CANZONERI (*Gazzetta*, 1897, **27**, ii, 1—5).—The fresh very fruity olive oil from puglia often possesses a markedly bitter taste, and burns the throat; the burning flavour of old rancid oil is somewhat similar to, but quite distinct from, this. The unpleasant flavour (technically termed "raspino") is lost on keeping the oil for some time, and the author has devised a method, which he will describe later, for removing it.

By distilling the oil in a current of steam, the author has separated from it an oil of the nature of camphene, to which olive oil probably owes its characteristic odour and taste, and eugenol, to which the burning flavour is doubtless due. It is noteworthy that Sobrero (*Annalen*, 1845, **54**, 88) obtained eugenol by distilling olivil, $C_{14}H_{18}O_5$. The author has also found catechin, catechol, gallic and tannic acids

and a new bitter substance, which in aqueous solution is coloured red by ammonia and violet by ferric chloride, in the faulty oils examined, though not all together in the same sample; the bitter flavour of the oil is attributable to these constituents.

The faulty oils in most, but not in all, cases, give Baudouin's reaction which is supposed to be characteristic of sesame oil; the author finds also that sesame oil does not always give this reaction. W. J. P.

Oil of Basil. By JULIUS BERTRAM and HEINRICH WALBAUM (*Arch. Pharm.*, 1897, **235**, 176—184).—The sample of oil from the island of Réunion possessing a sp. gr. $=0.954$ at 15° and a rotatory power $=+10° 12'$ (100 mm. tube) was first saponified, and the oil then fractionally distilled. Under 10 mm. pressure, it boils at 75—140°, the largest quantity distilling at 90—93°. In the various fractions, the presence of the following substances was proved. (1) Dextrorotatory pinene in the fraction of low boiling point (by preparing the nitrolbenzylamine compound by Wallach's method). (2) Cineol in the fraction boiling at 175—200°. The hydrobromide and Hirschsohn's iodol compound were obtained. The latter, $C_4I_4NH,C_{10}H_{18}O$, forms yellowish-green crystals, melts at 112°, can be crystallised from alcohol and benzene, is scarcely soluble in light petroleum, and is decomposed by sodium hydroxide with liberation of cineol. (3) Dextrorotatory camphor was found in the fraction which boils at 200—203° by preparing the oxime, and (4) methylchavicol in the large fraction boiling at 90—93°. Under atmospheric pressure, the last named portion boils at 215—216°, has a sp. gr. $=0.969$ at 15°, a rotatory power $+5° 57'$ (100 mm. tube), and a specific refraction $n_D=1.51371$ at 20°. This fraction, on oxidation with potassium permanganate, yielded anisic and homoanisic acids, and by treatment with sodium ethoxide, anethoil was prepared, hence the presence of methylchavicol was inferred. The original oil was found to contain 60 per cent. of this compound using Zeisel's methoxy-determination method.

A sample of German oil of basil had a different odour, a sp. gr. $=0.909$ at 15° and a rotatory power $=-21° 15'$ (100 mm. tube). The presence of cineol was proved, but no camphoroxime could be obtained from the oil. Homoanisic acid was prepared by oxidation, but the oil contained only 24·11 per cent. of methylchavicol. The oil must contain, however, a third alcoholic ingredient, for the fraction boiling at 200° on treatment with acetic anhydride, and subsequent titration with alcoholic potash gave a saponification number which indicated an alcoholic content of 40 per cent. $C_{10}H_{18}O$. This alcohol, in the light of Dupont and Guerlain's work on French oil of basil (this vol., i, 429), is probably linalool. E. W. W.

Isomeric Carvylamines. By HEINRICH GOLDSCHMIDT and ARMIN FISCHER (*Ber.*, 1897, **30**, 2069—2075).—Goldschmidt has shown that on reducing *d*-carvoxime with sodium amalgam, two isomeric carvylamines, $C_{10}H_{17}N$, are produced (Abstr., 1893, i, 723); the authors have examined the reduction products of *l*-carvoxime, and obtained the carbamide and benzoyl derivatives of the optical isomerides of the bases prepared originally. The corresponding racemic compounds have also been examined.

Benzoyl-α-d-*carvylamine* melts at 169° (*loc. cit.*); it is lævorotatory, and has $[\alpha]_D = -91\cdot9°$. *Benzoyl*-β-d-*carvylamine* has $[\alpha]_D = +176\cdot6°$. *Benzoyl*-α-l-*carvylamine* resembles the isomeride, and has $[\alpha]_D = +92\cdot6°$. *Benzoyl*-β-l-*carvylamine* has $[\alpha]_D = -175\cdot4°$. *Racemic benzoyl*-α-*carvylamine* crystallises in slender, white needles, melting at 141°, and *racemic benzoyl*-β-*carvylamine* in small prisms, melting at 140°; the latter is more readily soluble than the α-compound, and a mixture of the two isomerides melts at about 132°. M. O. F.

Constitution of Camphoric Acid. By LUIGI BALBIANO (*Ber.*, 1897, **30**, 1901—1909. Compare Abstr., 1896, i, 493, and this vol., i, 253).—The acid $C_8H_{12}O_5$, obtained from camphoric acid on oxidation, yields the *anhydride* when heated in a sealed tube with acetic anhydride; it is an amorphous substance, and when dissolved in benzene and heated with β-naphthylamine in a reflux apparatus, gives rise to the *β-naphthilic acid*, $COOH\cdot C_6H_{10}O\cdot CO\cdot NH\cdot C_{10}H_7$, which crystallises from alcohol in white leaflets, sinters at 168°, and melts and decomposes at 178°.

The acid $C_8H_{12}O_5$ resists the action of hydrochloric acid (sp. gr. = 1·19) when heated with it in sealed tubes at 130—140° during 12 hours; hydrobromic acid (sp. gr. = 1·50), under the same conditions, however, resolves the substance into trimethylsuccinic acid and carbonic oxide, and the same acid is produced under the influence of phosphorus pentachloride and pentabromide on solutions of the substance in phosphorus trichloride and tribromide. Hydrocyanic acid has no action on the compound.

The author summarises his previous work on the acid $C_8H_{12}O_5$, and states reasons for regarding Bredt's formula as an accurate representation of the constitution of camphoric acid. M. O. F.

Active Principles contained in the Bark of Periploca graeca. By EDUARD LEHMANN (*Arch. Pharm.*, 1897, **235**, 157—176).—The author describes in detail the methods used to isolate the bitter principle, *periplocin*, $C_{30}H_{48}O_{12}$, contained in the bark of this plant, which is found in the South-west Caucasus. It forms long, thin, colourless, transparent needles, melts at 205° forming a yellowish, viscous, transparent mass, and decomposes and evolves gas at 215°. It is easily soluble in ethylic and in amylic alcohols. At the ordinary temperature, 1 part dissolves in 125 of water, but it is less soluble in hot water; it is almost insoluble in ether, chloroform, benzene or light petroleum. The specific rotatory power $[\alpha]_D = +20°$. Its colour reactions and behaviour with various reagents are described in detail. On heating the glucoside periplocin with dilute sulphuric acid, *periplogenin*, $C_{24}H_{34}O_5$, is obtained together with a sugar which reduces Fehling's solution, but seems not to be identical with glucose. It is easily soluble in absolute alcohol, 70 per cent. alcohol, and chloroform, less soluble in ether, and insoluble in benzene and light petroleum. Water dissolves only 1 part in 2500, forming a bitter neutral solution. It crystallises in long, monoclinic prisms forming star-shaped groups, is unchanged at 100°, melts at 185° forming a thin, colourless liquid, and decomposes at 200°. The specific rotatory power $[\alpha]_D = +30°$. Its reactions are described in detail. Concentrated nitric acid oxidises both periplocin and periplogenin to a substance probably analogous

to trinitrophenol, since its yellow colour is unaffected by alkalis but becomes dark-red on the addition of potassium cyanide.

Attempts to isolate the odoriferous principle of the bark failed.

E. W. W.

Composition of the Root of Baptisia tinctoria. By K. GORTER (*Arch. Pharm.*, 1897, **235**, 301—320).—Baptisin can be extracted from the dried root by means of hot 60 per cent. alcohol, the extract, on evaporation, treatment with sodium hydroxide solution, and shaking with chloroform, yielding large quantities of a white, crystalline substance from which the glucoside can be readily obtained pure by recrystallisation from dilute alcohol. On extraction with chloroform, the alkaline filtrate yielded only small quantities of the alkaloid, but on acidifying the extracted liquid and precipitating with tannin, a second glucoside, *baptin*, was obtained melting at 188—189° after recrystallisation from alcohol. The alkaloid, *baptitoxine*, was obtained from the root, which had previously been extracted with alcohol, by treatment with dilute hydrochloric acid

Anhydrous *baptisin*, $C_{26}H_{32}O_{14}$, melts at 240° (uncorr.), and is lævorotatory $[\alpha]_D = -61° 40'$; it crystallises with $9H_2O$ from dilute alcohol, and on boiling with 16 per cent. sulphuric acid is split up into *baptigenin*, $C_{14}H_{12}O_6$ and rhamnose (isodulcitol); the former crystallises from dilute alcohol in white needles, which become brown at 250° without melting, and on treatment with sodium acetate and acetic acid yield a *triacetyl* derivative, consisting of white needles melting at 214—215° (uncorr.), and on benzoylation by the Baumann-Schotten method, a *monobenzoyl* derivative crystallising from alcohol in slender needles melting at 148°, and a *tribenzoyl* compound also consisting of slender needles melting at 208°. On bromination, baptisin yields a mixture of a dibromo- and a tribromo-derivative, the separation of which was not proceeded with. The presence of methoxy-groups in the glucoside could not be detected.

On nitration, baptigenin yields styphnic acid (trinitroresorcinol), which was identified by the formation of its *naphthalene* compound, which on crystallisation from acetone had the composition

$$C_6H_3N_3O_8,C_{10}H_8 + C_3H_6O;$$

it separates in yellow needles melting at 163·5° (uncorr.); it was not found possible to obtain the compound without acetone of crystallisation. On fusion with potash, both baptisin and baptigenin yield catechol, resorcinol and formic acid, together with a trace of guaiacol, and on oxidation with potassium permanganate, piperonal. When baptigenin is treated with a concentrated solution of sodium hydroxide, it is converted into *baptigenetin*, $C_{12}H_{10}O_4$, which crystallises in glistening, white plates melting at 148° (uncorr.); it is only slightly soluble in cold water, and, on acetylation, yields *diacetylanhydrobaptigenetin*, $C_{12}H_6O_3Ac_2$, a white, crystalline substance melting at 192—194° (uncorr.). None of the compounds above described have any physiological action.

Baptitoxine (cytisine), the alkaloid of the *Baptisia tinctoria*, R. Br, extracted by means of dilute hydrochloric acid, is present in the root in very small quantity. The *nitrate*, $C_{11}H_{14}N_2O,HNO_3 + H_2O$ (cytisine nitrate), crystallises from water in large, yellow crystals; it has a rotatory power $[\alpha]_D = -85° 52'$ at 17°, the free *base* melts at

152—153° (uncorr.) and has a rotatory power $[\alpha]_D = -118° 55'$ at 19°; the *hydrochloride* forms large, white crystals, and the *aurochloride*, which is anhydrous, reddish-brown needles melting at 212—213°.

J. F. T.

Constitution of Hydroxysantonin. By D. Lo Monaco (*Gazzetta*, 1897, **27**, ii, 87—95).—Jaffé (*Zeit. f. klin. Med.*, **17**, Supp., 7, and next abstract) found that santonin, when administered internally to dogs, is eliminated by the urine as a hydroxysantonin, $C_{15}H_{18}O_4$, and showed that this substance still contains the lactonic group present in santonin.

On administering to a dog 1 gram of santonin in meat paste every 24 hours, nothing abnormal is noticed during the first fortnight; after that time, however, the dog becomes emaciated, and each day, after taking the drug, is subject to convulsions of an epileptic nature, which become more intense as time goes on. The urine is yellow, changing to purple when rendered alkaline; the colour disappears after suspending the administration of santonin for 72 hours.

The α-hydroxysantonin separated from the urine is identical with Jaffé's preparation; it gives a *phenylhydrazone*, $C_{15}H_{18}O_3{:}N_2HPh$, which crystallises from boiling alcohol in transparent, yellow scales melting at 264—265°. *Acetyl-α-hydroxysantonin*, $C_{15}H_{17}O_4Ac$, obtained by boiling the santonin with acetic anhydride, crystallises in white scales melting at 164—165°.

The author concludes that α-hydroxysantonin probably has the constitution $\begin{matrix} CO\text{———}CMe{:}C\cdot CH_2\cdot CH\text{——}O \\ CH(OH)\cdot CMe{:}C\cdot CH_2\cdot CH\cdot CHMe \end{matrix}\!\!>\!CO.$

W. J. P.

Hydroxysantonin and its Production from Santonin in the Animal Body. By Max Jaffé (*Zeit. physiol. Chem.*, 1897, **22**, 538—555).—From the urine of dogs that have been fed on meat and given from 1—2 grams of santonin daily, *α-hydroxysantonin*, $C_{15}H_{18}O_4$, is obtained by evaporation, and extraction with alcohol. The residue from the alcoholic solution is treated with water and dilute sulphuric acid, and then extracted with ether, from which solvent the hydroxysantonin separates; the yield is from 5—6 per cent. of the santonin given.

α-Hydroxysantonin is sparingly soluble in boiling alcohol, chloroform and ether; slightly soluble in water, forming a neutral solution, and easily soluble in hot glacial acetic acid. From alcohol and chloroform, it separates in colourless, transparent, irregular plates, and from acetic acid in glistening scales which at 286° melt to a dark brown liquid, with disengagement of gas. Its solutions are strongly lævorotatory ($[\alpha]_D = -115°$).

α-Hydroxysantonin remains colourless, or at most becomes slightly yellow, when treated with alcoholic potash, whereas santonin, when similarly treated, becomes deep red; with sulphuric acid, it is coloured yellow, and on adding ferric chloride to the solution it acquires a pale violet colour which becomes clearer on warming, and then changes to a dirty yellowish-brown; the red colour produced with santonin under similar conditions, becomes an intense red-violet on warming.

α-Hydroxysantonic acid is obtained by adding sulphuric acid to a

solution of hydroxysantonin in sodium hydroxide. It forms an intensely acid solution, which on warming, and adding a dilute mineral acid, deposits crystals of *α-hydroxysantonic anhydride.* The latter substance readily takes up water to form the free acid, which in strongly alkaline solution has a rotatory power varying from $[\alpha]_D = -128{\cdot}5$ to $[\alpha]_D = -140{\cdot}4°$; and in neutral solution of $[\alpha]_D = -152°$.

The salts of this acid are readily soluble, the addition of soluble barium, calcium, silver, mercuric, and copper salts producing no precipitate. The *cadmium* compound, which appears to be a double salt containing varying amounts of cadmium, crystallises in clusters of needles. The *barium* salt formed by dissolving α-hydroxysantonin in baryta water, is a white powder easily soluble in water and alcohol.

α-Hydroxysantonin is readily oxidised by potassium permanganate or chromic acid, but owing to the small amount of material, the reaction could not be fully investigated, oxalic and hydrocyanic acids being the only substances identified.

On reduction with sodium amalgam, α-hydroxysantonin yields a substance which is probably *hydroxydihydrosantonin*, $C_{15}H_{20}O_4$, in spite of its marked acid character. It is a white powder, which could not be obtained in a crystalline condition; it is insoluble in water, almost so in benzene and light petroleum, but readily soluble in ether and chloroform. When heated in a capillary tube, it softens at 120—150° and changes gradually at 150—170° into a glassy, non-transparent, brown mass. In concentrated sulphuric acid, it dissolves with an intense cherry-red colour, which gradually changes to brown.

By the action of sodium amalgam on santonin, it was found impossible to obtain a compound of definite composition; the product is, however, very similar in properties to the one above described.

β-Hydroxysantonin, $C_{15}H_{18}O_4$.—Only very small amounts of α-hydroxysantonin could be found in the urine of rabbits to which santonin had been given, but from the ethereal extract the author isolated a new substance which he proposes to call β-hydroxysantonin. It is easily soluble in cold alcohol, ether, and chloroform, but insoluble in light petroleum. Under warm water, it melts to oily drops, which gradually dissolve, and on cooling separate again as plates melting at 128—131°. Its solutions are lævorotatory.

When dissolved in alcoholic potash, β-hydroxysantonin forms an orange-coloured solution, and in dilute sulphuric acid a yellowish-red solution, changing to dark green on addition of ferric chloride. When slowly melted, it changes to a yellow substance, which dissolves in sodium hydroxide with a beautiful red colour, but again turns yellow on acidification. This substance, which it was found impossible to obtain in a pure condition, is probably the yellow colouring matter usually found in urine.

The author suggests that artemisin, obtained by Merck (Abstr., 1896, i, 59) from the seeds of *Artemisia maritima*, as a bye-product in the separation of santonin, may be regarded as *γ-hydroxysantonin.*

A. W. C.

Benzylic Derivaties of the Santonous Acids and of Desmotroposantonin. By Nicola Castoro (*Rend. Accad. Linc.*, 1895, 4,

ii, 155—163. Compare Abstr., 1896, i, 306).—*Ethylic benzyldextrosantonite*,

$$\begin{array}{l} \qquad\qquad\;\; CH{:}CMe{\cdot}C{\cdot}CH_2{\cdot}CH_2 \\ \qquad\qquad\quad\;\; | \qquad\quad\;\; \| \qquad\;\; | \\ CH_2Ph{\cdot}O{\cdot}C{=\!=}CMe{\cdot}C{\cdot}CH_2{\cdot}CH{\cdot}CHMe{\cdot}COOEt \end{array}$$

, is prepared by the action of benzylic chloride on ethylic santonite in sodium chloride solution. It is readily hydrolysed by potash, giving the corresponding *acid*, which, although it could not be obtained crystalline, yields a very soluble *sodium* salt crystallising in needles.

Benzyl-levosantonous acid is obtained by reducing benzylisodesmotroposantonin with zinc dust and acetic acid; it does not crystallise, and seems to become racemic when heated at 100° in a vacuum.

W. J. P.

Lapachonone, a new Substance from Lapacho Wood. By F. CROSA and C. MANUELLI (*Rend. Accad. Linc.*, 1895, ii, 250—255). —On prolonged distillation in a current of steam, 2 kilos. of lapacho wood yielded a distillate from which 30 grams of a crystalline substance was separated by filtration; the filtrate, on extraction with ether, yielded a few grams of a heavy brown liquid of pronounced odour which boiled at about 180°. This liquid product was not further examined, but the solid, which the authors term *lapachonone*, has the composition $C_{16}H_{16}O_2$; it crystallises in colourless, orthorhombic laminæ melting at 61·5° and the above composition is supported by cryoscopic determinations in benzene and acetic acid. Its solutions are colourless, but rapidly become yellow on exposure to sunlight; if the coloured solutions be kept in the dark, however, they again become colourless. Lapachonone is optically inactive in benzene solution. When crystallised from alcohol with a molecular proportion of picric acid, a *compound* of the composition $C_{16}H_{16}O_2,C_6H_2(NO_2)_3{\cdot}OH$, melting at 145°, separates, but on recrystallisation from alcohol a new *compound*, of the composition $2C_{16}H_{16}O_2,3C_6H_2(NO_2)_3{\cdot}OH$, melting at 155°, is deposited, and on again recrystallising, the latter is converted into a *compound* of the composition $C_{16}H_{16}O_2,4C_6H_2(NO_2)_3{\cdot}OH$ melting at 153°; these substances form almost black, thin needles.

Lapachonone is slowly oxidised by dilute nitric acid, yielding phthalic acid, and is converted into a *dichlorolapachonone*, $C_{16}H_{14}Cl_2O_2$, by treatment with phosphorus pentachloride; the new substance crystallises in large, colourless, monosymmetric prisms melting at 108°, and is volatile in a current of steam. W. J. P.

Bixin. By KARL G. ZWICK (*Ber.*, 1897, **30**, 1972).—A preliminary paper, in which the author describes the method he has employed for the preparation of bixin in a crystalline condition. J. F. T.

Compounds from Lichens. By OSWALD HESSE (*Ber.*, 1897, **30**, 1983—1989. Compare Abstr., this vol., 1897, i, 255, where, on p. 257, for *Candelaria concolor*, read *Xantharia candelaria*).—*Candelaria concolor* contains no calycin (Zopf, Abstr., 1895, i, 298), but only dipulvic acid. Nor is calycin contained in *Gasparrinia medians* (*Physcia medians, Amphiloma medians*); the compound contained in these lichens resembles rhizocarpic acid, but is distinct from that substance.

The compound obtained, in addition to ethylic hæmatommate, when

atranorin is heated with ethylic alcohol, and formerly held (*loc. cit.*) to be methylphysciol, is now shown to be physcianin; as these are the only two products, the formula for hæmatommic acid must be changed to $C_8H_7O_3 \cdot COOH$, and atranorin must be regarded as the methylic salt of a lactonic acid, its decomposition by alcohols being represented by the equation

$$\underset{\text{Atranorin.}}{C_{17}H_{15}O_6 \cdot COOMe} + R \cdot OH = \underset{\text{Physcianin.}}{C_8H_9O_2 \cdot COOMe} + \underset{\text{Alkylic hæmatommate.}}{C_8H_7O_3 \cdot COOR}$$

The lichen collected from the bark of the American *Calisaya*, and which contains atranorin ("parmelin") together with a very little vulpic acid, certainly was *Parmelia perlata*; specimens collected at Feuerbach, it is true, contained neither vulpic nor usnic acids. Atranorin further occurs with capraric, physodic, and an amorphous acid in *Parmelia physodes* (*P. ceratophylla*), and with vulpic acid in *Evernia vulpina*; in *E. furfuracea* and *P. stellaris* var. *adscendens*, Th. Fr., it occurs alone.

Caperin and caperidin occur in *P. caperata* collected from the bark of oaks, but not in samples collected from fruit trees or granite rocks. This lichen also contains, in addition to usnic and caperatic acids, *capraric acid*, $C_{24}H_{20}O_{12}$, which crystallises in white needles that darken at 240—260°; it has a bitter taste, contains no alkoxy-group, and yields no acetyl derivative when treated with acetic anhydride, but instead, *anhydrocapraric acid*, $C_{24}H_{18}O_{11}$, which is reconverted into capraric acid by sodium carbonate.

The two compounds obtained by Zopf (this vol., Abstr., 1897, i, 437) from *P. ceratophylla* (*P. physodes*), in addition to atranorin, were probably capraric and physodic acids. Physodic acid, $C_{20}H_{22}O_6$, crystallises in white needles, and melts and decomposes at 190—192°; it contains no alkoxyl group; when boiled with baryta water, it loses carbonic anhydride (1 mol.). Neither capraric nor physodic acid yields ceratophyllin when treated with water, alcohol, or sodium carbonate, so that the atranorin must have been the source of the ceratophyllin (which melts at 147°, not 141°) previously obtained from the lichen in question. Ceratophyllin, physcianin and atraric acid are identical; they are methylic betorcinolcarboxylate. Gerding's physodin, obtained from *P. physodes*, was probably a mixture of atranorin and capraric acid.

Nephromium lusitanicum does not contain emodin, but a yellowish-brown crystalline substance, $C_{16}H_{12}O_6$, melting at 195°, to which the name *nephromin* is given. Presumably, it stands in the same relation to physcion as does emodin to chrysophanic acid. C. F. B.

Constitution of Inorganic Compounds. No. VIII. Anderson's Reaction. By ALFRED WERNER and FR. FASSBENDER (*Zeit. anorg. Chem.*, 1897, **15**, 123—142).—The characteristic reaction, known as *Anderson's reaction*, which takes place when the platinochlorides of organic bases are heated, is explained by referring these compounds to the type of metallic ammonium compounds. In the case of the pyridine compounds, the intermediate compound which is formed is a pyridine salt of the acid radicle $PtPyCl_5$. The following results are in accordance with this view.

Pyridine pentachloropyridineplatinate, $HPyPtPyCl_5$, [$Py = C_5NH_5$], a derivative of Anderson's intermediate compound, is easily obtained by warming the aqueous solution of pyridine platinochloride for a short time; it crystallises in large, yellow leaflets. The corresponding alkali salts cannot be obtained in a state of purity by the action of caustic alkalis alone, since the pyridine which is liberated at once reacts with the salts to form the final product of Anderson's reaction. They are, however, easily obtained by gradually adding a solution of the caustic alkali to an alcoholic solution of the pyridine salt containing ten times the theoretical quantity of methylic iodide necessary to combine with the pyridine which is liberated. The *potassium* salt, $KPtPyCl_5$, crystallises from hot water, in which it is easily soluble, in thin leaflets. The molecular conductivity is in accordance with the view that the salt is a compound containing a univalent negative ion. The solution slowly decomposes, and with a dilution of 512 litres after 5 minutes $\mu = 85$, after 480 minutes $\mu = 335$; hydrolysis takes place with the formation of potassium chloride and the acid $PtPyCl_4OH_2$. The *rubidium* salt, obtained in a similar manner to the potassium salt, crystallises from hot water in bright yellow leaflets, which under the microscope are seen to be formed of needles having a vertical fracture and a high double refraction; the solution slowly decomposes in a similar manner to that of the potassium salt. The *cæsium* salt crystallises in microscopic, short, rhombic needles which have a high double refraction. The *sodium* and *lithium* salts, unlike the preceding, contain water of crystallisation, and are easily soluble in alcohol, so that they cannot be prepared by the above method. They are obtained by adding sodium or lithium platinochloride respectively, to a solution of the potassium salt; the filtered solution is then evaporated to dryness and the salt extracted with absolute alcohol. The sodium salt crystallises from water in lustrous, orange-red, rhombic needles, shows a strong double refraction, and is very hygroscopic. The lithium salt crystallises in lustrous, orange-yellow needles.

Trichloropyridine platinites, $MPtPyCl_3$, are obtained by warming pyridine platinosochloride, $Py_2H_2PtCl_4$; they are the compounds corresponding to the above salts in the platino-series.

Potassium trichloropyridineplatinite, $KPtPyCl_3$, is obtained by heating the aqueous solution of pyridine hydrochloride (2 mols.) with potassium platinosochloride (1 mol.) on the water bath until the solution becomes orange-yellow. On concentrating the solution, a mixture of the potassium and pyridine salt is obtained. This mixture is suspended in alcohol, an excess of methylic iodide added, and then a concentrated solution of potassium hydroxide; the sparingly soluble potassium salt thus obtained is washed with alcohol, and crystallised from water, when it is obtained in orange needles having a strong double refraction. The molecular conductivity agrees with that required by the above formula. The aqueous solution, however, quickly undergoes hydrolysis with the formation of potassium chloride and the acid $PtPyCl_2OH_2$. The *rubidium* salt is obtained by adding hydrogen platinochloride to a solution of the potassium salt and adding alcohol; the filtrate which contains the acid $HPtPyCl_3$ is then treated with rubidium chloride, evaporated to dryness, and the residue

extracted with water ; it crystallises in orange, lustrous needles having a high double refraction. The *cæsium* salt, obtained in a similar manner to the rubidium salt, crystallises in lustrous, orange-yellow, rhombic needles.

The final product of Anderson's reaction is obtained by the action of pyridine on the above compounds. By the action of pyridine on the salts of pentachloropyridineplatinic acid, *platinum-tetrachlorodipyridine*, $PtPy_2Cl_4$, is obtained; this crystallises in small, sulphur-yellow needles. By the action of piperidine, a quantitative yield of the *compound* $PtPyPipCl_4$ is obtained ; it is a bright yellow, crystalline powder and is insoluble in water. Platinum-dichlorodipyridine, $PtPy_2Cl_2$, is obtained by the action of pyridine on potassium trichloropyridineplatinite, whilst by the action of piperidine the corresponding *compound*, $PtPyPipCl_2$, is formed.

The reversal of Anderson's reaction takes place easily and a theoretical yield of pyridine platinochloride, Py_2,H_2PtCl_6, is obtained when platinum tetrachlorodipyridine is heated with concentrated hydrochloric acid in a sealed tube at 180°. E. C. R.

3-Hydroxyquinoline-4-sulphonic Acid. By ADOLPH CLAUS and ALEXANDER KAUFMANN (*J. pr. Chem.*, 1897, [ii], **55**, 509—524. Compare Abstr., 1890, 523).—This acid is the sole product when 3-hydroxyquinoline is sulphonated. The normal *calcium* salt $(OH\cdot C_9NH_5\cdot SO_3)_2Ca + 2H_2O$; *barium*, with $2H_2O$; anhydrous *silver* ; *lead*, with $\frac{1}{2}H_2O$; and *cobalt* salt, with $\frac{1}{2}H_2O$, were prepared ; also the basic *sodium* salt, $ONa\cdot C_9NH_5\cdot SO_3Na + 1\frac{1}{2}H_2O$, and *potassium* salt, with $1\frac{1}{2}H_2O$. No ethereal salt could be obtained, the action of methylic iodide on the silver salt yielding the free acid and an alkylene, whilst alcoholic hydrochloric acid gives the free acid and the alkylic chloride. The *sulphonic chloride* was obtained as a brown oil which would not solidify ; the *sulphonamide* crystallises in white needles and melts at 69—70°. Fusion with potash at 275—280° converts the sulphonic acid into a brown, amorphous substance, which melts and decomposes at about 310°, and is presumably 3 : 4-*dihydroxyquinoline*. Oxidation with potassium permanganate converts the acid into quinolinic (2 : 3-pyridinedicarboxylic) acid ; the same product can be obtained by effecting the oxidation with dilute nitric acid, but in this case the sulphonic is certainly first replaced by the nitro-group. When 1 gram of the sulphonic acid is heated with about 20 c.c. of nitric acid of sp. gr. 1·11 for 2 hours in a sealed tube, the main product is nitro-3-hydroxyquinoline if the temperature is 130—140°, quinolinic acid being produced at 150—160°. It was found impossible to introduce any more substituting groups, such as iodine or bromine, into 3-hydroxyquinoline-4-sulphonic acid ; the sulphonic group is always removed first. The two bromine derivatives previously described (*loc. cit.*) are now respectively shown to be the yellow *hydrobromide* of 3-*hydroxy*-4-*bromoquinoline* (which itself melts at 186°), and a mixture of this with unchanged sulphonic acid, from which it is not easily freed. C. F. B.

Methyl-loretine and Lorenite. By ADOLPH CLAUS and ADOLPH KAUFMANN (*J. pr. Chem.*, 1897, [ii], **55**, 524—541).—*Methyl-loretine*

(*2-iodo-1-hydroxy-3-melthylquinoline-4-sulphonic acid*) is prepared by the following series of reactions: $C_9NH_6Me \rightarrow SO_3H \cdot C_9NH_5Me \rightarrow OH \cdot C_9NH_5Me \rightarrow OH \cdot C_9NH_4Me \cdot SO_3H \rightarrow OH \cdot C_9NH_3IMe \cdot SO_3H$. It crystallises with $1H_2O$, decomposes at 185—220° when heated, and is, generally, decidedly less stable than loretine itself; when oxidised with permanganate, it yields 2:3-pyridinedicarboxylic acid. The *sodium* salt, $OH \cdot C_9NH_3IMe \cdot SO_3Na$, also the *potassium*, with $\frac{1}{2}H_2O$; *ammonium*; *calcium*; *barium*, with $1H_2O$ (with $3H_2O$ when air-dried only?); and *strontium* salts, with $1H_2O$, were prepared. The basic salts of the same metals (except ammonium), $ONa \cdot C_9NH_3IMe \cdot SO_3Na$, &c., were likewise obtained; of these, the potassium salt crystallises with $\frac{1}{2}H_2O$, whilst the others are anhydrous. The normal salts are orange-coloured, and decompose at about 160—170°; the basic salts decompose at about 270—300°, and are colourless.

Lorenite (*3-iodo-4-hydroxyquinoline-1-sulphonic acid*) is prepared by sulphonating 4-hydroxyquinoline and iodising the product. It is isomeric with loretine, and resembles it, rather than methyl-loretine, in the degree of its stability; it decomposes at 210—230°; its normal salts are red and decompose between 190° and 250°, whilst the basic salts decompose at a higher temperature and are colourless or yellowish-white. The normal *sodium* (with $5H_2O$ when air-dried?); *potassium*, with $2H_2O$; *calcium*, with xH_2O; *barium*; and *strontium* salts, with xH_2O, were prepared; also the corresponding basic salts, with respectively 4, x, 4, O, and xH_2O.

When either loretine, methyl-loretine, or lorenite is applied externally as a drug, no iodine is present in the urine; it is found, however, in the form of both iodides and organic iodine derivatives when either of these drugs is taken internally, and its presence is indicated by the liberation of iodine when nitric acid is added to the urine. In order to liberate all the iodine from loretine or methyl-loretine, 6—8 times as much nitric acid must be used as will liberate completely the same amount of iodine present originally in the form of a metallic iodide.

C. F. B.

Ethylic Dicarboxylglutaconate. By SIEGFRIED RUHEMANN and A. S. HEMMY (*Ber.*, 1897, **30**, 2022—2031. Compare Trans., 1891, 743).—When ethylic dicarboxyglutaconate is treated with an excess of benzylamine, *ethylic benzylamidoethylenedicarboxylate*,

$$CH_2Ph \cdot NH \cdot CH \colon C(COOEt)_2,$$

is produced, and crystallises in colourless prismatic plates melting at 73—74°. Diethylamine unites with ethylic dicarboxyglutaconate to form a *salt*, $CH(COOEt)_2 \cdot CH \colon C(COOEt)_2, NHEt_2$, which crystallises in yellow needles and decomposes at 130°. When heated with diethylamine at 100°, *ethylic diethylamidoethylenedicarboxylate*,

$$NEt_2 \cdot CH \colon C(COOEt)_2,$$

is produced, which is a yellow, ethereal oil, of sp. gr. = 1·0435 at 28°/28°, and boils at 188° under a pressure of 15 mm. Piperidine behaves in a similar manner, forming a yellow, crystalline salt, which when heated with piperidine yields *ethylic piperidylethylenedicarboxylate*, as a viscid, yellow oil boiling at 223—224° under a pressure of 16 mm. Paraphenylenediamine reacts with ethylic dicarboxyglut-

aconate in the same mannner as metaphenylenediamine (Abstr., 1895, i, 334), *ethylic paraphenylenediamidodiethylenetetracarboxylate*, $C_6H_4[NH{\cdot}CH{:}C(COOEt)_2]_2$, being produced, which crystallises in yellowish-green, silky needles melting at 164—165°. Orthophenylenediamine, on the other hand, only reacts with 1 molecule of the ethylic salt, *ethylic orthophenylenediamidoethylenedicarboxylate*,

$$NH_2{\cdot}C_6H_4{\cdot}NH{\cdot}CH{:}C(COOEt)_2,$$

being formed. It crystallises in faintly yellow prisms melting at 92—93°. *Ethylic a-orthotolylenediamidoethylenedicarboxylate*, is obtained in a similar manner and crystallises in yellowish prisms melting at 145—146°.

The phenylpyrimidone melting at 207—208° (phenylhydroxypyrimidine), obtained by Ruhemann and Hemmy (this vol., i, 488) by the decomposition of 4-hydroxy-2-phenylpyrimidine-5-carboxylic acid, $CPh{<}{\begin{smallmatrix}N=\!=CH\\N\cdot C(OH)\end{smallmatrix}}{>}C{\cdot}COOH$, should be identical with that obtained by Pinner from 6-hydroxy-2-phenyl-4-carboxylic acid (*Die Imidoäther*, Berlin, 1892, 257), although the latter gave the melting point as 199°. The following derivatives may serve to characterise this compound more fully. 4-*Ethoxy-2-phenylpyrimidine*, $CPh{<}{\begin{smallmatrix}N=\!=CH\\N\cdot C(OEt)\end{smallmatrix}}{>}CH$, is readily obtained by the action of ethylic iodide on the hydroxy-compound, and forms a colourless oil which boils at 180° under a pressure of 24 mm., has the sp. gr. = 1·1204 at 19°/19°, and possesses a blue fluorescence. It forms a colourless, crystalline *hydrochloride* and a *platinochloride* which decomposes at 200°. 4-*Chloro-2-phenylpyrimidine*, $CPh{<}{\begin{smallmatrix}N:CH\\N\cdot CCl\end{smallmatrix}}{>}CH$, obtained by the action of phosphorus pentachloride on the hydroxy-compound, crystallises in colourless plates melting at 74°; it dissolves in concentrated hydrochloric acid, and yields a yellow, crystalline *platinochloride*, $(C_{10}H_7N_2Cl)_2,H_2PtCl_6$. Alcoholic ammonia at 150° converts the chloro-derivative into 4-*amido-2-phenylpyrimidine*, which crystallises with $\frac{1}{2}H_2O$ in colourless, compact prisms, and melts at 138—139° after losing its water at 120°; the anhydrous compound forms an amorphous mass, which takes up water from the air. The *hydrochloride* is readily soluble, and the *platinochloride* decomposes at 225°. The *acetyl* derivative crystallises in prismatic plates melting at 174—175°, and yields a *platinochloride*, which decomposes at 258°. The *benzoyl* derivative crystallises in colourless plates melting at 141°, and is insoluble in dilute acids.

A. H.

Cumenylimido-ethers. By PHILIPP FLATOW (*Ber.*, 1897, 30, 2006—2010).—*Cumenylimidoethyl ether hydrochloride*,

$$C_9H_{11}{\cdot}C(OEt){:}NH,HCl,$$

is formed when paracuminonitrile is treated with alcoholic hydrogen chloride. It melts at 98°, ethylic chloride being evolved and cuminamide produced, which then solidifies and melts again at 150°. All attempts to prepare the free imido-ether were unsuccessful.

Cumenylimidopropyl ether hydrochloride crystallises in slender, yellow, needles, which melt and decompose at 108°.

Cumenylamidine hydrochloride, $C_9H_{11}\cdot C(NH_2)\colon NH,HCl$, is produced by the action of alcoholic ammonia on the hydrochloride of the imido-ether, and crystallises in colourless tablets which melt at 190°. The *platinochloride* melts at 210°, the *picrate* at 195°.

2-*Paraisopropylphenyl*-4-*methyl*-6-*hydroxypyrimidine*,

$$C_6H_4Pr\cdot C{<}{N=CMe \atop N\cdot C(OH)}{>}CH,$$

obtained by treating cumenylamidine hydrochloride with caustic soda and ethylic acetoacetate, crystallises in colourless needles which melt at 165°, and are soluble both in acids and alkalis.

6-*Hydroxy*-2-*paraisopropylphenyl*-4 : 5-*dimethylpyrimidine*, which is prepared from ethylic methylacetoacetate, crystallises in long, silky needles melting at 208°. 6-*Hydroxy*-2-*paraisopropylphenyl*-4-*phenylpyrimidine*, $C_6H_4Pr\cdot C{<}{N=CPh \atop N\cdot C(OH)}{>}CH$, forms thin, silky needles melting at 227°.

Ethylic 6-*hydroxy*-2-*paraisopropylphenylpyrimidine*-4-*acetate*,

$$C_6H_4Pr{<}{N\colon C(CH_2\cdot COOEt) \atop N\text{———————}C(OH)}{>}CH,$$

is prepared by the use of ethylic acetonedicarboxylate, and crystallises in long, thin, silky needles melting at 128°.

6-*Hydroxy*-2-*paraisopropylphenylpyrimidine*-4-*carboxylic acid* is prepared from ethylic oxalacetate, and separates from alcohol in small scales which melt and decompose at 266°. 6-*Hydroxy*-2 : 4-*diparaisopropylphenylcyanidine*, $N{<}{C(C_6H_4Pr)\cdot N \atop C(C_6H_4Pr)\colon N}{>}C\cdot OH$, obtained by the action of phosgene on the amidine, crystallises in yellowish plates, with a satiny lustre, and melts at 253°.

2 : 4-*Diparaisopropylphenyl*-6-*methylcyanidine*,

$$N{<}{C(C_6H_4Pr)\cdot N \atop C(C_6H_4Pr)\colon N}{>}CMe,$$

is formed by the action of acetic anhydride on the amidine. It crystallises in slender needles and melts at 68°. A. H.

Existence of Condensation Rings with Para-linkage. By FRANZ FEIST (*Ber.*, 1897, **30**, 1982—1983. Compare Ladenburg, this vol., i, 485).—The author was unable to obtain a para-linkage by treating 2 : 5-dimethylpiperazine, $NH{<}{CH_2\cdot CHMe \atop CHMe\cdot CH_2}{>}NH$, with ethylenic iodide or bromide, stilbene bromide, benzaldehyde, formaldehyde, carbonyl chloride, or carbon bisulphide. In the last case, the product was the bisdithiocarbamate, $C_4N_2H_6Me_2(CSSH)_2$, which melts at 205°; this forms no para-linking when treated with ethylenediamine, neither does the dinitrosamine, when reduced; the dinitramine, curiously enough, yields the dinitrosamine when it is allowed to remain in contact with acetic anhydride. C. F. B.

Action of Phosphorus Chloride on Rosindone and Aposafranone. By OTTO FISCHER and EDUARD HEPP (*Ber.*, 1897, **30**, 1827—1831).—When rosindone (1 mol.), dissolved in five times its weight of phosphorus oxychloride, is treated with phosphorus pentachloride (1 mol.), the product is a reddish-yellow, crystalline substance,

with metallic lustre. This substance is readily decomposed by alkalis, and even by aqueous sodium acetate, rosindone being regenerated; when it is treated with potassium bromide or iodide, chlorine (? 1 atom) is displaced by bromine or iodine, whilst potassium nitrate throws down a sparingly soluble nitrate; with gold and platinum chlorides, it yields respectively a reddish-yellow *aurochloride* and a yellow *platinochloride*, both of which are anhydrous. It has thus the character of a salt, and must be regarded as *chloronaphthophenazonium chloride*,

$$C_{10}H_5Cl{<}\genfrac{}{}{0pt}{}{N\text{———}}{NPhCl}{>}C_6H_4,\ [N:N:Cl=1:2:4].$$

With aniline in alcoholic solution, it yields phenylrosinduline, and with ethylamine and methylamine respectively it yields ethylrosinduline and *methylrosinduline*; the last, $C_{23}H_{17}N_3$, melts at 180—181°; all of them have a greenish surface lustre.

Aposafranone, when treated in a similar fashion, yields *chlorophenylphenazonium chloride*, $C_6H_3Cl{<}\genfrac{}{}{0pt}{}{N\text{———}}{NPhCl}{>}C_6H_4$, [N : N : Cl = 1 : 2 : 4]. This forms brownish-yellow crystals with a bluish surface lustre, and resembles the compound described above in its chemical properties. With aniline, it yields *phenylaposafranine*, $C_{24}H_{17}N_3$, which crystallises in dark prisms with a bronze-like lustre, and melts at 201°. C. F. B.

Action of Hydrazine on Imido-ethers. By ADOLF PINNER (*Ber.*, 1897, **30**, 1871—1890. Compare Abstr., 1893, i, 710; 1894, i, 385; 1895, i, 136 and 270).—As a rule, the following compounds can be isolated from the products obtained by the action of hydrazine on an imido-ether, $R'O{\cdot}CR{:}NH$. (1)—The monhydrazidine, $NH_2{\cdot}CR{:}N{\cdot}NH_2$, obtained by the direct addition of hydrazine to the imido-ether and the subsequent elimination of a molecule of alcohol. (2)—The dihydrazidine, $NH_2{\cdot}CR{:}N{\cdot}N{:}CR{\cdot}NH_2$, formed by the addition of a molecule of the imido-ether to the monhydrazidine, and the subsequent loss of a molecule of alcohol. (3)—The dihydrotetrazine, $RC{<}\genfrac{}{}{0pt}{}{NH{\cdot}NH}{N\text{———}N}{>}CR$, formed by the action of free hydrazine on the monhydrazidine. (4)—The dihydrotriazole, $RC{<}\genfrac{}{}{0pt}{}{-NH-}{N{\cdot}NH}{>}CHR$, formed by the oxidation of the monhydrazidine, water, nitrogen, and ammonia being liberated. (5)—The triazole, $RC{<}\genfrac{}{}{0pt}{}{NH}{N{\cdot}N}{>}CR$, formed at the expense of the dihydrazidine. (6)—The tetrazine, $RC{<}\genfrac{}{}{0pt}{}{N{:}N}{N{\cdot}N}{>}CR$, formed by the oxidation of the dihydrotetrazine. (7)—The isodihydrotetrazine, $RC{<}\genfrac{}{}{0pt}{}{NH{\cdot}N}{N{\cdot}NH}{>}CR$, obtained by the intramolecular transformation of the dihydrotetrazine.

Acetic anhydride and sodium acetate react with dihydrazidines, yielding triazoles and acetyltriazoles, and not the true acetyl derivatives of the dihydrazidines as previously stated.

2 : 5-*Diphenyldihydrotriazole*, $CPh{<}\genfrac{}{}{0pt}{}{-NH-}{N{\cdot}NH}{>}CHPh$, is the compound previously (Abstr., 1893, i, 711) described as dibenzimidine. It is readily soluble in alcohol and acetone, extremely sparingly in water

and melts at 137°. It possesses somewhat strong basic properties, and its *hydrochloride* and *nitrate* are sparingly soluble in cold water. The *diacetyl* derivative, $C_{14}H_{11}N_3Ac_2$, obtained by boiling the base with sodium acetate and acetic anhydride for several hours, crystallises from light petroleum in short, thick prisms, melts at 93°, and is readily soluble in most organic solvents. When diphenyldihydrotriazole is heated with hydrochloric acid (10—12 per cent.) for several hours at 100° and then at 150°, it is converted into a mixture of benzoic acid, benzaldehyde, and Curtius's benzalazine, $CHPh\cdot N\colon N\cdot CHPh$.

1 : 5 : 2-*Acetylparatolylmethyltriazole*, $C_6H_4Me\cdot C\ll\genfrac{}{}{0pt}{}{NAc}{N\cdot N}\gg CMe$, is obtained when tolenylhydrazidine hydrochloride is added to a hot mixture of sodium acetate (2 parts) and acetic anhydride (12 parts), and the whole is heated for an hour; it crystallises in transparent prisms melting at 112°, and is readily soluble in hot alcohol. When tolenylhydrazidine hydrochloride is boiled for 10—15 minutes with a large excess of formaldehyde, and the mixture is allowed to cool, *tolenyldimethylenehydrazidine*, $CH_2\colon N\cdot C(C_6H_4Me)\colon N\cdot N\colon CH_2$, separates in glistening needles melting at 193°.

[With Alfred Salomon.]—When free hydrazine ($1\frac{1}{2}$ mol.), obtained by the action of caustic potash (33 per cent.) on hydrazine sulphate, is mixed with β-naphthimido-ether hydrochloride and alcohol (a quantity equal to the water present), the mixture sets to a mass of crystals which can be separated after 24 hours, and the β-naphthenylhydrazidine freed from potassium sulphate and chloride by treatment with dilute hydrochloric acid, extracting any unaltered imido-ether with ether, and then rendering the acid solution alkaline. *β-Naphthenylhydrazidine*, $NH_2\cdot C(C_{10}H_7)\colon N\cdot NH_2$, which crystallises in yellowish plates, is only sparingly soluble in water, but dissolves readily in alcohol, acetone, and acids; it begins to melt at 160°, but immediately solidifies, and then melts again and decomposes at about 230°. The *picrate* crystallises in yellow needles melting at 202°. *β-Naphthenyldimethylenehydrazidine*, $CH_2\colon N\cdot C(C_{10}H_7)\colon N\cdot N\colon CH_2$, melts and chars at 277°. *β-Naphthenylbenzylidenehydrazidine*, $NH_2\cdot C(C_{10}H_7)\colon N\cdot N\colon CHPh$, which crystallises in flat, yellowish needles melting at 96°, yields a *picrate* also crystallising in yellow needles. *β-Naphthenylcinnamylenehydrazidine*, $NH_2\cdot C(C_{10}H_7)\colon N\cdot N\colon CH\cdot C_8H_7$, melts at 170°, and yields a *picrate* melting at 180°. The monhydrazidine when heated with acetic anhydride yields *naphthoylhydrazide*, $C_{10}H_7\cdot CO\cdot NH\cdot NH_2$, crystallising in needles and melting at 186°. When a mixture of acetic anhydride and anhydrous sodium acetate is used, the chief product is 1 : 5 : 2-*acetyl-β-naphthylmethyltriazole*, $C_{10}H_7\cdot C\ll\genfrac{}{}{0pt}{}{NAc}{N\cdot N}\gg CMe$, which crystallises in colourless needles melting at 135°. *β-Naphthyltetrazole*, $C_{10}H_7C\ll\genfrac{}{}{0pt}{}{NH\cdot N}{N{-\!-}N}$ (with the two N on the right joined by a double bond), prepared by adding sodium nitrite to a solution of the hydrazidine hydrochloride, crystallises in colourless prisms melting and decomposing at 203°. It is readily soluble in alcohol, ether, or acetone, yields an *ammonium* derivative, $C_{11}H_7N_4\cdot NH_4$, crystallising in colourless plates and melting at 210°, also *lead*, *silver*, *methyl*, and *ethyl* derivatives, the last two melting at 112° and 55° respectively.

Dinaphthenylhydrazidine, $NH_2\cdot C(C_{10}H_7){:}N\cdot N{:}C(C_{10}H_7)\cdot NH_2$, is the chief product obtained by the action of hydrazine (1 mol.) on naphthimido-ether ($1\frac{1}{2}$ mol.). It is only sparingly soluble in the usual solvents, but crystallises from aniline in yellow, glistening plates; it melts at 246°, but is converted at the same time into the tetrazole. It possesses very feeble basic properties; when suspended in acetone and treated with concentrated hydrochloric acid, it yields a *hydrochloride*, $C_{22}H_{18}N_4,2HCl$, which is readily decomposed by water. The *nitrate* is a white powder which melts at 122°, with rapid evolution of gas. Sodium nitrite and hydrochloric acid have no action on the dihydrazidine.

Naphthenylbenzenylhydrazidine, $NH_2\cdot CPh{:}N\cdot N{:}C(C_{10}H_7)\cdot NH_2$, is obtained by the addition of free benzimido-ether to an alcoholic solution of naphthenylhydrazidine. The base is sparingly soluble in alcohol, cold acetone, or mineral acids, with the latter of which it forms salts. When heated, it decomposes and then melts at the same temperature as the triazole. 2 : 5-*Naphthylphenyltriazole*, which is most readily obtained by heating the preceding compound with glacial acetic acid, crystallises from alcohol in colourless prisms melting at 217°, and yields a white precipitate with silver nitrate. *β-Naphthenylparatolenylhydrazidine* melts at 202°, and the corresponding 2 : 5-*naphthylparatolyltriazole* at 190°. 2 : 5-*Dinaphthyltriazole*, obtained from the dihydrazidine on boiling it with acetic acid, melts at 222°; it yields a crystalline *silver* salt and an *acetyl* derivative melting at 187°. *Dinaphthyldihydrotetrazine* crystallises in thin, orange-coloured needles which are readily oxidised to the tetrazine. It has the same melting point as the tetrazine, and is sparingly soluble in alcohol. The *diacetyl* derivative, $C_{22}H_{14}N_4Ac_2$, crystallises in colourless prisms melting at 210°. *Dinaphthyltetrazine* crystallises in broad, flat, red needles melting at 246°, and sparingly soluble in benzene, readily in acetone or ethylic acetate. When boiled for 5—6 hours with aqueous potassium hydroxide, it yields *naphthoyl-β-naphthylidenehydrazide*, $C_{10}H_7\cdot CH{:}N\cdot N{:}C(OH)\cdot C_{10}H_7$.

2 : 5-*Dinaphthyldihydrotriazole* is obtained in a crystalline form when aqueous potassium hydroxide is added to an alcoholic solution of naphthenylhydrazidine and the mixture is allowed to stand for 6—8 weeks. It forms large, yellow plates, which are practically insoluble in the usual solvents with the exception of boiling glacial acetic acid. It melts and decomposes at 240°, yields a *diacetyl* derivative, $C_{22}H_{15}N_3Ac_2$, melting at 138°, and when heated at 150—160° with glacial acetic acid yields β-naphthoic acid and *β-naphthalazine*, $C_{10}H_7\cdot CH{:}N\cdot N{:}CH\cdot C_{10}H_7$, melting at 162°.

[With GÖBEL.]—No monhydrazidine can be obtained by the action of hydrazine on phenylacetimido-ether, $CH_2Ph\cdot C(OEt){:}NH$, the chief product being *diphenylacetohydrazidine*,

$$NH_2\cdot C(CH_2Ph){:}N\cdot N{:}C(CH_2Ph)\cdot NH_2,$$

which crystallises from alcohol in yellowish plates melting at 153°. The *hydrochloride*, $C_{16}H_{18}N_4,HCl$, and *nitrate*, $C_{16}H_{18}N_4,HNO_3$, are described. 2 : 5-*Dibenzyltriazole*, obtained by boiling the above dihydrazidine for a short time with glacial acetic acid, crystallises in plates melting at 147°, and yields a *silver* salt decomposing at 170°.

Dibenzyldihydrotetrazine crystallises from alcohol in reddish needles,

and, when freshly prepared, melts at 158—160°, but after it has been kept for some time, it melts at a much lower temperature, owing to partial conversion into the tetrazine. When warmed with hydrochloric acid, the dihydrotetrazine is readily transformed into *dibenzylisodihydrotetrazine* melting at 162°; the latter is, however, always accompanied by a certain quantity of the hydrazide of phenylacetic acid. The *hydrochloride* and *nitrate*, $C_{16}H_{16}N_4,HNO_3$, of the isodihydrotetrazole and also a *diacetyl* derivative, melting at 93°, are described.

Diphenylacetohydrazide, $CH_2Ph\cdot CO\cdot NH\cdot NH\cdot CO\cdot CH_2Ph$, crystallises in needles melting at 231°.

Dibenzyltetrazine, which crystallises from dilute alcohol in long, flat prisms melting at 74°, is readily soluble in the usual organic solvents with the exception of light petroleum.

The imido-ether, $OH\cdot CHPh\cdot C(OEt)\colon NH$, obtained from mandelonitrile, when treated with hydrazine, yields neither a monhydrazidine nor a dihydrazidine, the chief product being *dihydroxydibenzyldihydrotetrazine*, $OH\cdot CHPh\cdot C\lessgtr\!\begin{matrix}NH\cdot NH\\ N\text{———}N\end{matrix}\!\gtrless C\cdot CHPh\cdot OH$, which crystallises in yellowish needles melting at 193°. It yields a *tetracetyl* derivative melting at 203°. J. J. S.

Action of Hydrazodicarbonamide on Hydrazine Sulphate. By Attilio Purgotti (*Gazzetta*, 1897, **27**, ii, 60—67).—On heating a mixture of hydrazine sulphate and hydrazodicarbonamide in an oil bath at 210—215°, ammonia and hydrogen sulphide are evolved, and on extracting with water, filtering and evaporating the solution, *paraurazine* or *paradiketohexahydrotetrazine*, $CO\lessgtr\!\begin{matrix}NH\cdot NH\\ NH\cdot NH\end{matrix}\!\gtrless CO$, separates in small, colourless, brilliant, monosymmetric crystals melting and decomposing at 266—267° [$a:b:c = 1\cdot159:1:?$; $\beta = 87°\ 55'$]. Paraurazine has the normal molecular weight in boiling aqueous solution, and reduces ammoniacal silver nitrate in the cold, but is stable towards Fehling's solution; it behaves as a monobasic acid, giving a white *silver* salt, $C_2O_2N_4H_3Ag$. W. J. P.

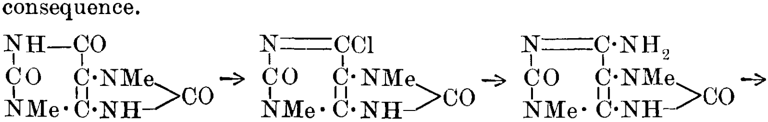
Action of Hydrazine on Cumenylimido-ether. By James Colman (*Ber.*, 1897, **30**, 2010—2011).—When the hydrochloride of cumenylimido-ether is treated with potassium carbonate and an alkaline solution of hydrazine sulphate, a precipitate is formed on standing which contains two compounds. Of these, *dicumenylhydrazidine*, $NH_2\cdot C(C_9H_{11})\colon N\cdot N\colon C(C_9H_{11})\cdot NH_2$, is insoluble in acetone but soluble in alcohol. It crystallises in yellow, lustrous plates, melts at 193°, and when boiled with acetic acid, is converted into 2 : 5-*diparaisopropylphenyltriazole*, $C_9H_{11}\cdot C\lessgtr\!\begin{matrix}NH\\ N\cdot N\end{matrix}\!\gtrless C\cdot C_9H_{11}$, which crystallises in thin, colourless plates, and melts at 210°. The second compound is the corresponding *hydrazo*-derivative, which has not been obtained pure, since it oxidises in the air, forming *diparaisopropylphenyltetrazine*, $C_9H_{11}\cdot C\lessgtr\!\begin{matrix}N\colon N\\ N\cdot N\end{matrix}\!\gtrless C\cdot C_9H_{11}$, which crystallises in deep red plates melting at 156—157°. The filtrate from these two compounds contains *cumenylhydrazidine*, $C_9H_{11}\cdot C(NH_2)\colon N\cdot NH_2$, which has not

itself been isolated, but is converted by sodium nitrite into *paraisopropylphenyltetrazole*, $C_9H_{11}\cdot C\Big\langle\begin{matrix}NH\cdot N \\ N - N\end{matrix}$, which crystallises in long needles or broad plates melting at 189°. The *ammonium* and *barium* salts are both crystalline. The *methyl* derivative crystallises from alcohol in colourless plates melting at 120—122°. A. H.

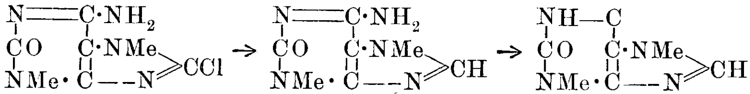
Action of Hydroxylamine on Ethylic Dicarboxyglutaconate. By SIEGFRIED RUHEMANN (*Ber.*, 1897, **30**, 2031—2032. Compare Abstr., 1897, i, 445).—The researches of Claisen (this vol., i, 493), Uhlenhuth (*ibid.*, i, 444), and Rabe (*ibid.*, i, 568), show that the product formed by the action of hydroxylamine on ethylic dicarboxyglutaconate is identical with that formed by the action of hydroxylamine on ethylic ethoxymethylenemalonate, and has the constitution of ethylic isoxazolonecarboxylate, $COOEt\cdot C\Big\langle\begin{matrix}CO\cdot O \\ CH\cdot NH\end{matrix}$. A. H.

Action of the Electric Current on some Alkaloids. By HERBERT POMMEREHNE (*Arch. Pharm.*, 1897, **235**, 364—368).—Caffeine when decomposed by the electric current yields amalic acid, formic acid, ammonia, and methylamine, whilst morphine, when submitted to the same treatment, gives rise to oxydimorphine, and quinine to thalleioquinine. J. F. T.

Synthesis of Theobromine. By EMIL FISCHER (*Ber.*, 1897, **30**, 1839—1845).—3 : 7-Dimethyluric (γ-dimethyluric) acid has now been prepared synthetically (this vol., i, 268), and from it dimethyldioxychloropurine (chlorodioxydimethylpurine) can be obtained by the combined action of phosphorus pentachloride and oxychloride (Abstr., 1896, i, 13). The product of the latter reaction, when heated at 130° with four times its weight of aqueous ammonia (saturated at 0°) for 3 hours in a sealed tube, yields 6-*amido*-2 : 8-*dioxy*-3 : 7-*dimethylpurine*; when heated, this decomposes without melting. It forms salts with acids, and also yields sodium, potassium, and ammonium derivatives, the latter of which is decomposed on the water bath. When heated for 4 hours at 170° with ten times its weight of phosphorus oxychloride, it yields 8-*chloro*-6-*amido*-2-*oxy*-3 : 7-*dimethylpurine*, which crystallises with $3H_2O$, decomposes without melting, when heated, and has basic properties. This substance, when warmed with four times its weight of hydriodic acid of sp. gr. 1·96 and a little powdered phosphonium iodide, is reduced to 6-*amido*-2-*oxy*-3 : 7-*dimethylpurine*, which crystallises with $3H_2O$, decomposes when heated, and is still unmelted at 380°, and has basic properties; when dissolved in dilute sulphuric acid, and heated with sodium nitrite, it yields theobromine, to which the formula given below must be assigned in consequence.



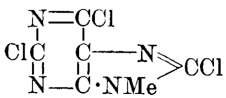
3 : 7-Dimethyluric acid. 6-Chloro-2 : 8-dioxy-3 : 7-dimethylpurine. 6-Amido-2 : 8-dioxy-3 : 7-dimethylpurine.



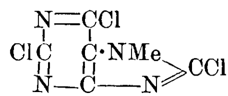
8-Chloro-6-amido-2-oxy-3 : 7-dimethylpurine. 6-Amido-2-oxy-3 : 7-dimethylpurine. Theobromine.

C. F. B.

The Two Methyltrichloropurines. By EMIL FISCHER (*Ber.*, 1897, **30**, 1846—1859; for the nomenclature compare this vol., i, 268, where the 8 and 9 should be interchanged).—Both 9- and 7- (formerly α- and β-; Abstr., 1884, 996, and 1896, i, 13) methyltrichloropurine react



Trichloro-9-methylpurine (α).



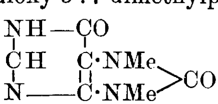
Trichloro-7-methylpurine (β).

with alkalis, the 9 compound more easily, and yield the same products as when they react with hydrochloric acid, one Cl being exchanged for OH, and an 8-oxy compound formed. With alcoholic potash, two chlorine atoms are attacked, and diethoxy-compounds are formed; the second chlorine atom attacked is certainly in the 6-position in the case of the 7-methyl compound, and presumably so in the case of the other. These ethoxy-compounds can be hydrolysed to the oxy-compounds by heating with strong hydrochloric acid on the water bath, whilst with hydriodic acid and phosphonium iodide, the remaining chlorine atom can be replaced by hydrogen.

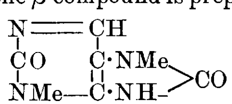
Aqueous potash acts on trichloro-7-methylpurine at the ordinary temperature, but more rapidly at 100°, yielding 2 : 6-dichloro-8-oxy-7-methylpurine. Alcoholic potash at 3° forms 2 : 6-*dichloro*-8-*ethoxy*-7-*methylpurine*, melting at 185—186° (corr.); at 35—40°, it forms 2-*chloro*-6 : 8-*diethoxy*-7-*methylpurine*, which melts at 194—195° (corr.), yields a *chloromethyloxyethoxypurine* melting at 270—271° (corr.), when hydrolysed with hydriodic acid, and 6 : 8-*dioxy*-7-*methylpurine* when reduced with hydriodic acid and phosphonium iodide; the last named substance turns brown at about 400°, or melts if heated rapidly, and has both acid and basic properties.

Aqueous potash acts on trichloro-9-methylpurine only at the boiling temperature, and even then 2 : 6-dichloro-8-oxy-9-methylpurine is not the only product. Alcoholic potash at 5° forms 2 : 6-*dichloro*-8-*ethoxy*-9-*methylpurine*, which melts at 154° (corr.); at the boiling temperature it forms *chlorodiethoxy*-9-*methylpurine* (presumably 2-chloro-6 : 8-diethoxy-), which melts at 149—150° (corr.), and when hydrolysed with hydrochloric acid yields a product melting at 264°.

The compounds formerly known as α- and β-dimethyldioxypurine (*loc. cit.*) can now be identified respectively as 6 : 8-dioxy-7 : 9-dimethylpurine and 2 : 8-dioxy-3 : 7-dimethylpurine. For the β-compound is prepared by



6 : 8-Dioxy-7 : 9-dimethylpurine (α).



2 : 8-Dioxy-3 : 7-dimethylpurine (β).

reducing the dimethyldioxychloropurine obtained from 3 : 7-dimethyluric acid (compare synthesis of theobromine, this vol., i, 641). And the α-isomeride is known to be an 8-oxy compound. These compounds can be methylated by heating them with aqueous potash and methylic iodide in a sealed tube at 100°. They yield respectively 6 : 8-*dioxy-1 : 7 : 9-trimethylpurine*, which melts at 235—236° (corr.), and can also be obtained by methylating 6 : 8-dioxy-7-methylpurine; and 2 : 8-*dioxy-3 : 7 : 9-trimethylpurine*, which melts at 254° (corr.). Both of these substances have basic properties; the *aurochloride* of the first contains water of crystallisation (?, $2H_2O$), that of the second is anhydrous; both differ from caffeine in that they do not give the murexide test after treatment with chlorine water.

[With Friedrich Jacobi.]—When an alcoholic solution of 7-methyltrichloropurine is saturated with ammonia, 2 : 6-*dichloro-8-amido-7-methylpurine* is formed. This decomposes at a high temperature without melting; it has basic properties, and dissolves also in alkalis; when reduced with hydriodic acid and phosphonium iodide on the water bath, it forms 8-*amido-7-methylpurine*, which decomposes without melting completely, and is basic in character; when hydrolysed with strong hydrochloric acid in a sealed tube at 120—130°, it yields 8-*amido-2 : 6-dioxy-7-methylpurine*, which has both basic and acid properties (the *sodium* salt, $C_6H_6N_5O_2Na + 2H_2O$, was analysed), and is oxidised by warm nitric acid to alloxan, in consequence of which it gives the murexide test. C. F. B.

Ammonium Bases of the Morphine Group. By Eduard Vongerichten (*Annalen*, 1897, **297**, 204—220.)—*Bromodiacetylmorphine*, $C_{21}H_{22}BrNO_5$, is obtained by treating diacetylmorphine suspended in water with an aqueous solution of the calculated amount of bromine; the perbromide at first precipitated gradually disappears, and bromodiacetylmorphine separates on adding sodium carbonate to the reddish-brown liquid. It crystallises in colourless prisms, and melts at 208°.

Bromomorphine, $C_{17}H_{18}BrNO_3$, produced by the action of alcoholic sodium methoxide on the foregoing substance, crystallises from alcohol in small prisms; when precipitated by alkalis from aqueous solutions of its salts, bromomorphine forms a crystalline powder containing $\frac{1}{2}H_2O$, and softens at 120°. The substance does not dissolve in the calculated amount of sodium hydroxide, and, unlike morphine, requires considerable excess of the alkali for dissolution; when treated in alcoholic solution with sodium ethoxide and methylic iodide, one-half remains unchanged, a very small proportion undergoing conversion into bromocodeine, the remainder yielding a mixture of methiodides. A solution of bromomorphine in dilute nitric acid does not yield a precipitate when heated with silver nitrate at 90°; on adding a few drops of the concentrated acid, however, silver bromide is precipitated after a short interval, nitromorphine being probably formed. Oxidising agents which convert morphine into pseudomorphine have no effect on bromomorphine under the same condition. The *hydrochloride* crystallises from water in white needles containing $3H_2O$, and is less readily soluble in water than morphine

hydrochloride; the *methiodide* crystallises from water in colourless prisms containing $1H_2O$, and melts and decomposes at 252°. The *methoxide* forms slender needles, and when treated with methylic alcohol and methylic iodide yields the *methiodide* of bromocodeine, which contains $1H_2O$; it crystallises in stellar aggregates of prisms, and melts at 242—244°.

Bromomethylmorphimethine, $C_{19}H_{22}BrNO_3$, is obtained by treating bromocodeine methiodide with alkalis, and crystallises from methylic alcohol in white leaflets; it melts at 132°, and remains turbid until 180°, when it becomes brownish, but if heated to 170—175°, and allowed to cool, it solidifies in white needles at 150—145°, and in this form melts at 182—184°. The solution in concentrated sulphuric acid is brownish-black, and becomes pale bluish-green after a time. The *platinochloride* contains $4H_2O$. *Acetoxymethoxybromophenanthrene*, $C_{17}H_{13}BrO_3$, is produced on heating bromomethylmorphimethine with acetic anhydride for several days in a reflux apparatus; it crystallises from methylic alcohol in stellate groups of needles, and melts at 166°.

Chlorocodide *methiodide*, $C_{18}H_{20}ClNO_2,MeI$, is prepared by dissolving chlorocodide in cold methylic iodide, separation of iodine occurring when the substances are heated. The *methohydroxide* is strongly alkaline, and gives no precipitate with silver nitrate; on boiling the aqueous solution, however, the liquid becomes neutral, and the addition of silver nitrate then produces a precipitate of silver chloride.

Bromodiacetylmorphine *methiodide* crystallises in stellate groups of needles containing $1\frac{1}{2}H_2O$; it softens at 185°, and melts at 200°, evolving gas. The *methohydroxide* is very unstable, and in aqueous solution becomes converted spontaneously into the acetate of bromacetylmorphine methohydroxide. When potassium iodide is added to the aqueous solution of this substance and the liquid concentrated, the *methiodide* of bromacetylmorphine is obtained in wedge-shaped plates containing $2H_2O$; it melts indefinitely and evolves gas at 215—220°. The *methohydroxide* of bromacetylmorphine is syrupy, and yields bromacetylcodeine methiodide when heated with methylic iodide and methylic alcohol.

Bromacetylcodeine *methohydroxide* is obtained from the methiodide, and yields the acetate of bromomethylmorphimethine when the aqueous solution is concentrated. Bromocodeine *methochloride* crystallises in silky needles, and contains $2\frac{1}{2}H_2O$; when heated with acetic anhydride on the water bath, it yields bromacetylcodeine methochloride, and on heating the aqueous solution of the corresponding methohydroxide, it becomes neutral, and contains bromomethylmorphimethine.

Acetylcodeine *methiodide* forms long, colourless needles melting and evolving gas at 250—252°; the *methohydroxide*, when heated in aqueous solution, is converted into the acetate of codeine methohydroxide.

M. O. F.

Action of Bromacetophenone on Strychnine. By HANS RUMPEL (*Arch. Pharm.*, 1897, **235**, 398—400).—If a solution of strychnine is added to a chloroform solution of bromacetophenone, a crystalline substance begins to separate immediately; this is *strychnine*

acetophenone bromide, $C_{21}H_{22}N_2O_2,C_6H_5·CO·CH_2Br + H_{2}O$, which crystallises in colourless needles melting at 245—250°; the corresponding *chloride*, prepared by treating the bromide with silver chloride, forms small nodules melting at 232—233°. J. F. T.

Alkaloids contained in the Seeds of Blue and White Lupins. By L. SHERMAN DAVIS (*Arch. Pharm.*, 1897, **235**, 199—240). See this vol., i, 174. E. W. W.

Alkaloids contained in the Seeds of Lupins. By ERNST SCHMIDT (*Arch. Pharm.*, 1897, **235**, 192—198).—A short *resumé* of previous investigations is given. In the seeds of *Lupinus luteus* and of *L. niger*, the author found lupinine, $C_{21}H_{40}N_2O_2$, and lupinidine, $C_8H_{15}N$. The molecular weight of the latter was determined by Raoult's method. The seeds of *L. perennis* contain dextrolupanine and another alkaloid not yet identified. E. W. W.

Lupinine and Lupinidine from Yellow Lupins. By L. BEREND (Marburg) (*Arch. Pharm.*, 1897, **235**, 262—289).—The alkaloids were extracted from the seeds of *Lupinus luteus* by means of alcoholic hydrochloric acid, the extract being made alkaline, extracted with ether, and the mixed alkaloids separated as mercurochlorides. *Lupinine*, $C_{21}H_{40}N_2O_2$, which crystallises from light petroleum in colourless needles or rhombic plates melting at 67—68°, is easily soluble in ether and chloroform; its specific rotation is $[\alpha]_D = -20$ in a 0·95 per cent. solution. The *platinochloride* forms yellow crystals melting at 163—164°, and the *aurochloride* glistening, transparent needles melting at 196—197°; the *hydrochloride*, in a 2 per cent. solution, gives $[\alpha]_D = -14°$. Bromine does not give rise to any definite bromo-derivative, whilst phosphoric anhydride and hydrochloric acid produce anhydrolupinine and *dianhydrolupinine*, $C_{21}H_{36}N$, the latter forming a dark red *platinochloride*; no trace of oxylupinine could be observed. On treatment with acetic anhydride, lupinine yields a *diacetyl* compound, the *aurochloride* of which melts at 120°. The presence of two hydroxyl groups in lupinine is shown by the formation of a well-defined although unstable *dichloro*-derivative, when it is treated with phosphorus pentachloride or phosphorus oxychloride; the *aurochloride* of this compound consists of stellate groups of needles. Like lupinine, dianhydrolupinine combines with 2 mols. of methylic iodide; the corresponding *aurochloride* melts at 180°.

Lupinidine, $C_8H_{15}N$, is a yellowish-brown oil having an agreeable ethereal odour when pure; the *sulphate* melts and decomposes at about 180°; the *platinochloride* crystallises with $2H_2O$ and melts at 227°, the *aurochloride* forms slender needles melting at 189°, and the *mercurochloride* is a white, crystalline powder which decomposes at 200°. The *hydriodide*, $C_8H_5N,HI + \frac{1}{2}H_2O$, which is most conveniently obtained by treating a solution of the hydrochloride with potassium iodide, consists of glistening plates; the *basic hydriodide*, $(C_8H_5N)_2,HI$, on the other hand, prepared by treating the alkaloid with hydriodic acid, or by the action of ethylic iodide on the hydrochloride, consists of transparent, rhombic prisms melting at 230°. J. F. T.

The Alkaloids of the Black Lupin. By K. GERHARD (*Arch. Pharm.*, 1897, **235**, 342—355).—A quantitative estimation of the alkaloids contained in the different varieties of lupin seeds gave the following results.

	Estimated as lupanine, $C_{15}H_{24}N_2O$.	as lupinine, $C_{21}H_{40}N_2O_2$.
Yellow	0·4493 per cent.	0·6378 per cent.
Blue	0·7249 ,,	—
White	1·1115 ,,	—
Perennial	1·1829 ,,	—
Black	0·6100 ,,	0·8659 ,,

The alkaloids extracted from the black lupins are the same as those derived from the yellow varieties, namely, lupinine and lupinidine. Various salts of these alkaloids obtained from the different varieties of lupin are described in detail (compare Berend, preceding abstract).

J. F. T.

Alkaloids of the Perennial Lupin (Lupinus polyphyllus) (*Arch. Pharm.*, 1897, **235**, 355—363), **and of other Species of Lupin** (pp. 363—364). By K. GERHARD.—The alkaloid derived from the seeds of *Lupinus polyphyllus* is identical with the dextrolupanine, $C_{15}H_{24}N_2O$, obtained from the seeds of the blue lupin by Davis (this vol., i, 174). The hydrochloride, hydriodide, platinochloride, aurochloride, and thiocyanate of the base are described.

The seeds of *L. affinis*, *L. albococcineus*, *L. Cruikshanksi*, *L. Moritzianus*, *L. mutabilis*, and *L. pubescens* were also examined; they all contained alkaloids, but they were not extracted in quantity sufficient to characterise them.

J. F. T.

Alkaloids of the Lupinus Albus. By ARTURO SOLDAINI (*Arch. Pharm.*, 1897, **235**, 368—374).—The main facts have already appeared (compare Abstr., 1896, i, 193).

J. F. T.

Cytisine. By J. LAMMERS (*Arch. Pharm.*, 1897, **235**, 374—397).—The alkaloid used for these investigations was obtained from the laburnum seed. *Dibromocytisine*, obtained from its hydrobromide, crystallises from absolute alcohol in fine white crystals melting at 65—73°, and yields the alkaloid on reduction, both in acid and alkaline solution (see baptitoxine, this vol., i, 627). *Bromocytisine*, which is formed on reducing the hydrobromide of the dibromo-derivative with zinc and acetic acid, is a brownish-yellow oil; the *hydrobromide*, $2(C_{11}H_{13}BrN_2O,HBr) + 3H_2O$, consists of colourless prisms; the *hydrochloride*, which crystallises with $2H_2O$ of fine, white prisms, the *platinochloride* $(C_{11}H_{13}BrN_2O)_2,H_2PtCl_6 + H_2O$ of yellow needles, the *aurochloride* of orange-red crystals melting at 217°, the *tartrate* of colourless plates, the *nitrate*, crystallising with $1H_2O$, in broad prisms. The *methiodide* crystallises in anhydrous, white needles, and the *methochloride* in fine, white crystals; the *aurochloride* of monobromomethylcytisine forms golden-yellow crystals, and the *platinochloride* brownish-red plates. *Methylcytisine*, $C_{11}H_{13}N_2O{\cdot}CH_3$, obtained from the methiodide by treating it with potassium hydroxide, yields *dibromomethylcytisine hydrobromide* on bromination; this separates from its warm, aqueous

solution in slender needles melting at 197—198°. The corresponding *hydrochloride* forms fine, white crystals, and the *platinochloride* yellow needles stable at 250°.

Dibromocytisine methiodide, $C_{11}H_{11}Br_2N_2O{\cdot}CH_3,HI$, crystallises in white needles soluble in water, and on methylation gave rise to a compound identical with that prepared by the bromination of methylcytisine; the bromine atom cannot therefore have replaced the hydrogen in the imido-group of the alkaloid.

Dichlorocytisine is prepared by the chlorination of cytisine; its *hydrobromide*, $2(C_{11}H_{12}Cl_2N_2O,HBr) + H_2O$, crystallises in white needles, the *hydrochloride* in fine, anhydrous white needles, the *platinochloride*, in orange-yellow, soluble needles, and the *aurochloride* in red needles.

J. F. T.

Carpaine. By J. J. L. van Rijn (*Arch. Pharm.*, 1897, **235**, 332—342).—This is a preliminary paper, dealing with carpaine, the alkaloid, $C_{14}H_2NO_2$, extracted from *Carica papaya*, L. On methylation, it yields *methylcarpaine* crystallising from dilute alcohol in small, colourless prisms melting at 71°, benzoylation of nitrosocarpaine yields a colourless crystalline substance melting at 100°, and containing the nitroso-group unchanged; the alkaloid on oxidation with potassium permanganate in acid solution, gives rise to a variety of compounds which are still under investigation. The paper concludes with a crystallographic description of carpaine and its principal salts. J. F. T.

Biliverdic Acid, a Product of the Hydrolysis of the Colouring-matter of Bile. By William Küster (*Ber.*, 1897, **30**, 1831—1835). —Bilirubin, $C_{16}H_{18}N_2O_4$, was prepared from gall-stones by Maly's method. (This Journal, 1875, 651.) It was dissolved (1 mol.) in acetic acid, and treated gradually with a concentrated aqueous solution of sodium dichromate (equivalent to 6 atoms oxygen); only 3 atoms of oxygen reacted at 20°, the rest at 100°. Sulphuric acid equivalent to the sodium present was added, the acetic acid evaporated, and the residual liquid extracted with ether; from this extract, yellowish crystals of a substance, $C_8H_9NO_4$, were obtained. To this the name of *biliverdic acid* is given; it behaves like a monobasic acid with N/5 ammonia, but a neutral solution of the ammonium salt gives, with silver nitrate, a precipitate containing 2 atoms of silver in the molecule; it has, moreover, the character of an unsaturated compound, for it decolorises permanganate instantaneously in the cold; it evolves no ammonia when it is boiled with alkalis, neither has it any basic properties. The author inclines to the opinion that the nitrogen is present as a cyanogen group, in which case the substance might be nearly related to hæmatic acid, $C_8H_8O_5$, the product of the oxidation of hæmatoporphyrin (this vol., i, 232). C. F. B.

Deoxycholic acid. By Ernst Vahlen (*Zeit. physiol. Chem.* 1897, **23**, 99—108).—Some time since, the author described (Abstr., 1896, i, 453) a substance isolated from putrefied ox-bile, which he believed to be different from choleic acid and identical with the deoxycholic acid described by Mylius (Abstr., 1886, 481). By fractionally precipitating the bile with barium chloride, a salt is obtained yielding a free

acid which crystallises from glacial acetic acid in delicate prisms, melts at 140—145°, and on analysis gives numbers agreeing well with those required for deoxycholic acid.

As it is difficult to separate this acid from admixed choleic acid, experiments were made on the reduction of pure cholic acid, to ascertain if by this means a similar substance could be obtained.

When cholic acid is treated with zinc dust in acetic acid solution, an acid is obtained which crystallises from glacial acetic acid and melts at 140—145°. The barium salt crystallises in microscopic needles, is unlike the barium salt of choleic acid, and is apparently identical with the salt obtained from fermented ox-bile.

The acid melting at 140—145° is also obtained by reducing choleic acid in alkaline solution, and the author proposes to further investigate the exact composition of this substance. A. W. C.

Bromalbumin and its Behaviour towards Microbes. By Oscar Loew and S. Takabayashi (*Bull. Coll. Agric. Imp. Univ. Tokyo*, 1897, **3**, 237—240).—Bromalbumin (Abstr., 1885, 823) is now prepared by mixing equal weights of albumin and bromine, which must be cooled during the operation, and then heating the mixture at 60° for two days. The product is washed successively with water, sulphurous acid, dilute sodium carbonate, 50 per cent. alcohol, and absolute alcohol. The substance, dried at 100°, contains 10·64—11·0 per cent. of bromine.

Experiments with 1 per cent. solutions of bromalbumin, with and without peptone and cane-sugar respectively, showed that the compound is not favourable for the development of microbes (putrefaction microbes and bacilli of anthrax) in absence of air, even in presence of sugar, but does not prevent development in presence of peptone.

N. H. J. M.

Iodo-Derivatives of Proteids (Casein). By A. Liebrecht (*Ber.*, 1897, **30**, 1824—1826).—*Periodocasein* is obtained as a yellow powder by warming an intimate mixture of casein with a quarter of its weight of iodine on the water bath, and removing the excess of iodine by extraction with ether, or by boiling casein with 70 per cent. alcohol and iodine; it contains 17·8 per cent. of iodine, and dissolves in hot, dilute alcohol. When it is treated with an alkaline thiosulphate, and then washed with water, alcohol, and ether, it yields *iodocasein*, a white substance which contains 5·7 per cent. of iodine, is insoluble in the commoner solvents, and, like casein, has acid properties. If it is heated with about 20 times its weight of 10 per cent. sulphuric acid for 2 hours on the water bath, it yields *caseoiodin*, a white powder which contains about 8·7 (8·5—9·3) per cent. of iodine, has acid properties, gives the biuret reaction, and resembles iodothyrin in its physiological action. C. F. B.

// JOURNAL

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THE CHEMICAL SOCIETY.

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

PART II.

General and Physical Chemistry.

Indices of Refraction of Metals at different Temperatures. By A. PFLÜGER (*Ann. Phys. Chem.*, 1896 [2], **58**, 493—499).—Kundt, who determined the indices of refraction of a number of metals at different temperatures (Abstr., 1889, 749), came to the conclusion that the temperature coefficients for the indices of refraction are of the same order as the coefficients of the electrical conductivities of the metals, and that, therefore, the velocity of light at different temperatures in a given metal is directly proportional to the electrical conductivity. As this result is not in harmony with recent observations of the reflection of metals at different temperatures, the author has been led to repeat some of Kundt's determinations, using the metallic prisms formerly employed. The results obtained are not in agreement with those of Kundt, and are not found to support his conclusions with reference to the velocity of light and the electrical conductivity in metals. H. C.

Refractometric Researches. By JOHAN F. EIJKMAN (*Rec. Trav. Chim.*, 1896, **15**, 52—60).—The author calculates the molecular refractions for a number of the hydrocarbons of the paraffin series, making use of the formula which he has given in a previous paper $MV(n^2-1)/(n+0{\cdot}4)$. The change in the refraction and dispersion for every additional CH_2 group is constant from the sixth term, the values being for the lines $H\beta$, $H\alpha$, and A.

$\beta = 10{\cdot}431$ $\alpha = 10{\cdot}260$ $A = 10{\cdot}052$ $\beta - \alpha = 0{\cdot}171$

These numbers are independent of the temperature, and correct to within one unit of the third decimal. The calculated values for the two methyl groups or hydrogen atoms at the ends of the chain are then

	β	α	A	$\beta - \alpha$
CH_3	12·285	12·105	11·885	0·180
H_2	3·71	3·69	3·67	0·020

H. C.

Behaviour of Circularly Polarising Crystals in a State of Powder. By HANS HEINRICH LANDOLT. (*Ber.*, 1896, **29**, 2404—2412).—The specific rotation of isotropic circularly polarising crystalline substances may be determined in an ordinary polarimeter tube by suspending the finely-powdered material in a liquid of its own refractive index and measuring the angle through which the polarisation plane of the entering beam is deflected; the material is powdered in an agate mortar and sifted, the particles being preferably of 0·004—0·012 m.m. in diameter. The polarimeter tube should be rotated whilst the measurements are made in order to keep the powder in homogeneous suspension; the rotation may be either right or left-handed, but the number of revolutions per minute should be 50—80, because at higher speeds the solid particles are driven to the sides of the tube by centrifugal force and the readings thus made valueless. Several series of experiments were made with right and left-handed sodium chlorate, the powder being placed in a test tube with alcohol, and carbon bisulphide slowly added until the mixture was as transparent as possible; the mixture was then transferred to the polarimeter tube and, after the reading had been taken, the contents of the tube were evaporated to dryness in order to determine the weight of salt employed. The specific rotation of sodium chlorate was in this way determined as $[\alpha]_j = \pm 1·42°$ per m.m., practically the same value as is obtained with plates of the massive salt; it is thus evident that particles of sodium chlorate of 0·004—0·012 m.m. in diameter still possess the same crystalline structure as that to which the circular polarisation of the large crystals is due. W. J. P.

The Characteristics of Optically Isomeric Compounds. By HERMANN TRAUBE (*Ber.*, 1896, **29**, 2446—2447). Walden (Abstr., 1896, 553) has brought forward a number of substances which do not conform to Pasteur's rule that all substances which are optically active in solution crystallise in hemihedral forms. It must, however, be remembered that the crystallographic symmetry of none of these has been completely investigated. In most cases, the form has simply been determined, but no attempt has been made to ascertain the exact degree of symmetry of the crystal by the study of etch figures, the pyro-electric properties, etc. In every case which has thus been carefully examined, Pasteur's law has been verified. The same remarks apply to the exceptions to the rule that the crystal forms of two oppositely active modifications of a substance are enantiomorphous.

The author further points out that Becke (*Tschermak's Min. und*

petrogr. Mitthlg. 1889, **10**, 414; 1891, **12**, 256) has shown that Pasteur's rule can be directly deduced from the Le Bell-van't Hoff theory.

A. H.

Influence of Linking on the Rotatory Power. By PAUL WALDEN (*Zeits. physikal. Chem.*, 1896, **20**, 569—585).—A number of compounds were investigated to determine the relations between the optical properties of saturated and unsaturated compounds in both the aliphatic and aromatic series. The experimental results are given in the accompanying table, in which V = the molecular volume, R is the molecular refraction (Lorenz) observed, and $R_{(calc)}$ that calculated from Conrady's numbers, D is the molecular dispersion $(n_f - n_c)\,M/d$; $[M]$ the molecular rotation and S the difference in the latter for $-H_2$.

	V	R	R_{calc}	D	$[M]$	S
Amylic butyrate	181·82	45·41	45·39	1·153	+ 4·33°	2·29°
Amylic crotonate	174·15	45·62	45·00	1·69	+ 6·62°	
Amylic isobutyrate	183·32	45·42	45·39	1·151	+ 4·90°	·57°
Amylic methylacrylate	177·66	45·24	45·00	1·524	+ 5·47°	
Amylic succinate	268·98	70·04	70·28	1·926	+ 9·71°	5·46°
Amylic fumarate	264·03	70·89	69·89	2·487	+15·17°	
Amylic chlorosuccinate	283·6	75·27	75·23	2·178	+10·98°	5·80°
Amylic chlorofumarate	275·1	75·53	74·83	2·636	+16·78°	
Amylic methylsuccinate	285·5	74·53	74·88	2·31	+ 9·99°	6·02°
Amylic mesaconate	278·47	75·52	74·47	2·76	+16·01°	
Amylic tricarballylate	387·05	103·1	104·3	2·69	+15·48°	8·18°
Amylic aconitate	382·90	104·32	103·97	3·50	+23·66°	
Amylic phenylpropionate	226·32	65·07	65·13	2·603	+ 4·98°	11·38°
Amylic cinnamate	218·2	68·30	64·73	5·106	+16·36°	
Amylic phenylpropiolate	215·35	66·79	63·32	4·33	+12·05°	
Amylic α-naphthoate	228·19	74·55	71·44	5·43	+12·78°	9·83°
Amylic β-naphthoate	229·8	75·20	71·44	5·52	+22·61°	

From the above results, the author draws these conclusions:—The influence of the double linking as compared with the single linking is to cause:—(1) an increase in the density, and hence a decrease in the molecular volume; (2) an abnormal molecular refraction which is not only greater than the calculated value, but also greater than that of the allied singly linked compound; (3) a marked increase in the molecular dispersion and a great increase in the molecular rotation. The influence of the triple linking is similar to that of the double linking, but less marked. The naphthalene derivatives show anomalies in their optical properties, the rotation of the β-derivative being extraordinarily great.

L. M. J.

Luminescence. By W. ARNOLD (*Zeits. Kryst. Min.*, 1896, **27**, 92—93).—The phosphorescence observed by Pope (*Trans.*, 1895, **67**, 985) on crushing crystals of orthobenzoicsulphinide is termed triboluminescence in accordance with Wiedemann's suggestion.

The author has examined saligenin, benzophenone, benzoic acid

salicylic acid, gallic acid, tannin, hippuric acid, and vanillin for cathodoluminescence, thermoluminescence, and triboluminescence; hippuric acid, however, is the only one which shows triboluminescence. Orthobenzoicsulphinide shows no cathodoluminescence, and its triboluminescence is less marked than that of hippuric acid.

None of the substances named above show fluorescence on exposure to Röntgen rays, but are all quite transparent to them.

W. J. P.

Santonin and its Derivatives. By LUIGI BRUGNATELLI (*Zeits. Kryst. Min.*, 1896, **27**, 78—90. Compare Andreocci, this vol., i, 182). —The etch-figures produced by alcohol, ether, or ethylic acetate on rhombic crystals of optically active santonin indicate that the crystals are hemihedral.

On crushing crystals of ethylisodesmotroposantonin, a yellow phosphorescence is observed; similarly, crystals of dextro- and lævo-ethylic santonite and lævodesmotroposantonous acid exhibit a yellowish green phosphorescence, whilst crystals of lævoethyldesmotroposantonous acid show an emerald green phosphorescence on being crushed. The phosphorescence is of a similar kind to that observed by Pope on breaking crystals of orthobenzoicsulphinide (*Trans.*, 1895, **67**, 985).

No connection seems to exist between phosphorescence of this kind and optical activity, although the phenomenon is not observed with the racemic modifications of the substances mentioned above; a connection may possibly exist between the cleavage and the phosphorescence, since several substances exhibiting a good cleavage phosphoresce on trituration. Many substances, however, like phenacetin, which possess a good cleavage, do not phosphoresce, whilst others, which have no cleavage, like dichloromethylparatolylsulphone, show the phenomenon well. W. J. P.

Theory of Liquid Chains. By JOHAN M. LOVÉN (*Zeits. physikal. Chem.*, 1896, **20**, 593—600).—The difference of potential between two solutions was investigated for the case in which the anions are similar but the cations respectively univalent and bivalent. The equation obtained is

$$\pi_1 - \pi_2 = 0{\cdot}002\ T. \frac{3u_1 - 2u_2 + v}{3u_1 - 4u_2 - v} \log \frac{3\ (u_1 + v)}{4\ (u_2 + v)}$$

where u_1 and u_2 are the migration velocities of the univalent and bivalent cations, and v that of the anion. To test the validity of the expression, the E.M.F. was determined in the case of chains containing hydrogen chloride and chloride of barium, calcium, magnesium or zinc. In dilute solutions ($C_1 = 0{\cdot}01$), the agreement is satisfactory, but in more concentrated solutions ($C_1 = 0{\cdot}1$) the agreement is not good, probably owing to incomplete dissociation. L. M. J.

Peroxide Electrodes. By OLIN F. TOWER (*Zeits. physikal. Chem.*, 1896, **21**, 90—92).—Owing to an erroneous calculation, the values given in some of the tables of the author's previous paper (Abstr., 1896, ii, 142) are wrong. The corrected values are given in this paper, and when these corrections are made, it is seen that the values

for the hydrogen dissociation in acid organic salts obtained by the author do not agree with those of Trevor as previously stated.

L. M. J.

Peroxide Electrodes. By W. A. SMITH (*Zeits. physikal. Chem.*, 1896, 21, 93—107).—The author gives a short account of points in the preparation of the electrodes wherein he differs from Tower (Abstr., 1896, ii, 142). He finds also that, with many acids, constant values for the E.M.F. are not obtainable. In those acids which yield a constant E.M.F., the values for the dissociation calculated from the expression $\pi = 0{\cdot}02908 \,.\, \log m^4c^4/m'^4,c'^4$, do not agree with those obtained by other observers. Replacing the exponent 4 by a variable, x, and calculating back from the dissociation, values varying between 3·4 and 3·7 are obtained, but they are approximately constant for each of the acids and its salts. Hence by the use of the mean value 3·56 in place of 4, results are obtained in better accord with the dissociation. This, however, is probably only approximate, for the value varies with the acid ion; being however equal for the acid and the salt, it may be first obtained from the acid and then the hydrogen dissociation calculated for the acid salts. By this means, values are obtained in better accord with theoretical considerations and with the results of other observers than are those of Tower.

L. M. J.

Electrolytic Behaviour of Solutions of Salts and Acids in Methylic Alcohol. By NICOLAI D. ZELINSKY and SERGEI G. KRAPIWIN (*Zeits. physikal. Chem.*, 1896, 21, 35—52).—The authors determined the conductivity of a number of salts and acids in aqueous solution, and in methylic alcohol, employing Ostwald's modification of Kohlrausch's method. The bromides and iodides of potassium and ammonium behave in the alcoholic solution as strong electrolytes, the conductivity at $v = 512$ being only about 30 per cent. less than that in aqueous solution. Cadmium iodide has a very small alcoholic conductivity, the ratio, mv_2/mv_1 increasing with dilution. In the substituted ammonium compounds, such as tetramethylammonium bromide and iodide, tetrethylammonium iodide, ethylmenthylamine hydrochloride and nitrate, the conductivity differed only slightly in the two solvents. Ethylenediamine hydrochloride is also fairly strongly dissociated in alcohol. Hydroxylamine hydrochloride exhibits, in aqueous solution, a rapid increase of the value mv_2/mv_1 owing to decomposition of the compound into acid and base, but this does not occur in the alcoholic solution. Tin diethyl- and triethyl-iodides behave in alcohol as weak electrolytes and obey the dilution law; the addition of water to the former markedly raises the conductivity, probably owing to decomposition. It is noticeable that oxalic and iodic acids behave also as very weak electrolytes. In dimethylsuccinic acid, the conductivity is found to be almost proportional to the volume. (Comp. Trevor, Abstr. 1893, ii, 62), whilst trichloracetic acid is found to obey the dilution law in methylic alcohol, a result previously obtained for ethylic alcohol by Wildermann (Abstr. 1894, ii, 375). The addition of water, not only in small but also in large quantities, diminishes the conductivity of the alcoholic solutions of alkali bromides, &c. Thus

the solution containing 50 per cent. of water has a conductivity about 0·7 of that in alcohol and about 0·5 of that in water. L. M. J.

Melting Points of Aluminium, Silver, Gold, Copper and Platinum. By SILAS W. HOLMAN, R. R. LAWRENCE and L. BARR (*Phil. Mag.*, 1896 [5], **42**, 37—51).—With the help of a platinum and rhodo-platinum thermo-couple, the authors have determined the melting points of a number of pure metals. With the exception of the platinum, the metals used were all of a high degree of fineness. The absolute values obtained depend in part on the assumption of 1072° as the melting point of pure gold (Holborn and Wien, Abstr., 1896, ii, 87). The numbers are offered as provisional only, but with the belief that they are more trustworthy than previous data.

Aluminium	660°	Copper	1095°
Silver	970°	Platinum	1760°

H. C.

Determination of Specific Heats by means of the Electric Current. By A. SCHLAMP (*Ann. Phys. Chem.*, 1896, [2], **58**, 759—770). —Pfaundler has shown that if a current is sent through the resistances ω_1 and ω_2 placed in calorimeters which contain the quantities m_1 and m_2 of liquids of the specific heats c_1 and c_2,

$$\frac{m_1\, c_1\, \Delta t_1 + r_1\, \Delta t_1}{m_2\, c_2\, \Delta t_2 + r_2\, \Delta t_2} = \frac{\omega_1}{\omega_2}$$

where r_1 and r_2 are the water equivalents of the vessels, stirrers, &c. and Δt_1 and Δt_2 are the corrected rises in temperature. In using this method for specific heat determinations, the specific heat of one of the liquids used must be known and that of the other can then be calculated.

The author has determined the specific heats of the following substances in the liquid state at temperatures above 90°, the specific heat of turpentine being deduced from Regnault's determination and used as the standard of reference.

	Sp. Heat.	Temperature.	Mol. Heat.
Turpentine	0·5055	93°	—
Nitrobenzene	0·4023	93	49·48
Aniline	0·5378	92·5	50·03
Benzene	0·4814	94	37·55
Naphthalene	0·4272	94·5	54·68
α-Naphthylamine	0·4756	94·2	68·01
Nitronaphthalene	0·3900	94·3	67·47
Paratoluidine	0·5335	94·1	57·05
Phenol	0·5610	93·9	52·73
Orthotoluidine	0·5364	94·0	57·40

H. C.

Specific Heat of Viscous Sulphur. By J. DUSSY (*Compt. rend.*, 1896, **123**, 305—308).—Sulphur contained in a thin glass bulb was heated to the desired temperature, and the bulb was then lowered into a thin glass tube of somewhat greater diameter contained in the calorimeter, and allowed to cool under these conditions. In some of the experiments, after the temperature had fallen below 157°, the

bulb containing the sulphur was broken, and the contents allowed to mix with the water. These precautions were taken in order to prevent the formation of plastic sulphur in an indefinite condition. The following results were obtained.

Temperature	160–201°	160–232·8°	160–264°	201–232·8°	232·8–264°
Mean specific heat	0·279	0·300	0·300	0·331	0·324

The curve representing the loss of heat between a given temperature T and 0° seems to change in direction at about 230°.

Vitreous Sulphur.—When tempered between 157° and 175°, sulphur solidifies very rapidly, and has a characteristic vitreous appearance. Sulphur heated to 220°, poured suddenly into cold water, and allowed to cool in contact with it, yields an outer layer of plastic sulphur, an intermediate layer of vitreous sulphur, and an inner core of the prismatic variety. This vitreous form seems to be the analogue of the well-known vitreous selenium. C. H. B.

Specific Heats at Constant Volume of the C_nH_{n2+2} Hydrocarbons. By ADOLFO BARTOLI and ENRICO STRACCIATI (*Gazzetta*, 1896, **26**, i, 472—474).—The determination of the coefficients of compressibility, K_t (this vol. ii, 9), renders it now possible to calculate the specific heats, C, at constant volume of these hydrocarbons by Thomson's formula—

$$c = C - \frac{10336\, T(v_o\delta_t)^2}{E\, K_t\, v_t},$$

in which C is the specific heat at constant pressure, v_t the specific volume at the temperature $t = 23°$, T the absolute temperature $273° + t°$, δ_t the coefficient of thermal expansion and E the mechanical equivalent of heat. The principal values concerned, namely, c, C and C/c, are tabulated in the abstract referred to. The authors conclude that whilst the specific heats at constant pressure of the C_nH_{2n+2} hydrocarbons are practically the same, the specific heats at constant volume increase as the molecular weight rises; the ratio C/c of the two specific heats increases regularly as the molecular weight decreases, but never attains the value 1·41 which the ratio has in the case of gases.
W. J. P.

Selection of the Unit of Heat. By ADOLFO BARTOLI (*Gazzetta*, 1896, **26**, i, 475—482).—The author discusses the various units of heat in use, and concludes that it would be most convenient to define the thermal unit as the quantity of heat necessary to raise the temperature of 1 kilo. of water at 15° by 1° of the normal nitrogen thermometer of the *Sèvres bureau international des poids et mesures.*
W. J. P.

Cyanic Acid. By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1896, **123**, 337—341).—When a strong acid is added to an alkali cyanate the first thermal disturbance is due to the displacement of the cyanic acid, but this is followed by a further disturbance due to transformations of the liberated cyanic acid.

With acetic acid and potassium cyanate, the early development of heat amounts to 1·05 Cal., and it follows that the heat of neutralisation of cyanic acid is + 12·25 Cal. With hydrochloric acid, the results are less distinct, owing to the rapid transformation of the cyanic acid, but they tend to confirm that obtained with acetic acid. Boric acid gives no thermal disturbance, and this also indicates that the heat of neutralisation of cyanic acid is about 12·0 Cal. Adopting 12·25 Cal. as the heat of neutralisation, it follows that

$$C + N + H + O + Aq. = HCNO \text{ diss. develops } + 37{\cdot}0 \text{ Cal.}$$
$$HCN \text{ diss.} + O = HCNO \text{ diss.} \qquad + 61{\cdot}4 \text{ Cal.}$$

The conversion of cyanic acid into ammonium hydrogen carbonate develops + 24·0 Cal.

The addition of ammonium chloride to potassium cyanate solution absorbs − 0·2 Cal., and it follows that the heat of neutralisation of cyanic acid by ammonia is about + 10·7 Cal. The heat of formation of ammonium cyanate from its elements is + 68·9 Cal., and the conversion of dissolved ammonium cyanate into carbamide will develop 8·3 Cal. C. H. B.

Thermodynamical Surfaces of a Substance in the Solid and Liquid States. By GUSTAV TAMMANN (*Zeits. physikal. Chem.*, 1896, **21**, 17—34).—In an ordinary thermodynamical surface, a break occurs at the change from liquid to solid state. The effect is considered of employing in place of the parameter p the value for the actual internal pressure $p+k$, and calculations are made on the assumption that this would give one thermodynamical surface without breaks. The relation $(dv'/dp) > (dv''/dp)$ is deduced (where v' refers to solid and v'' to liquid), and this is in accord with the experiments of Barus on the compressibility of solid and liquid naphthalene. The inequality $(dv'/dT) > (dv''/dT)$ is also obtained, a result which is also proved by the experimental evidence available. The continuity of the surface cannot, however, be assumed in case of such compounds as wax, alloys, &c., which have no definite melting-point, or in which two or more classes of molecular groups exist. The paper concludes with a discussion of the forms of the curve representing melting point/pressure in different classes of compounds, a maximum occurring in these cases where $v' > v''$ and a minimum also if $v' < v''$. L. M. J.

Specific Gravities of Mixtures of Normal Liquids. By CHARLES E. LINEBARGER (*Amer. Chem. J.*, 1896, **18**, 429—453).—The author terms those liquids "normal," which, as indicated by the work of Guye, Ramsay and Shields, and others, are formed from their vapours without any change in molecular condition. If the degree of molecular association of liquids be taken as a basis of classification, three classes of binary mixtures may be distinguished.

1. The liquids mixed are normal;
2. One liquid is normal, the other associated;
3. Both liquids are associated.

Mixtures of the first class may be expected to exhibit the simplest behaviour in respect to their physical properties, and as the mixing of

normal liquids is not attended by any change in the number of molecules present, it becomes of interest to inquire what changes of volume occur when such liquids are mixed. For this purpose, the densities of a number of binary mixtures of normal liquids have been determined with all possible care. The liquids chosen were benzene, toluene, chlorobenzene, nitrobenzene, ether, ethylic acetate, ethylic iodide, ethylic benzoate, carbon bisulphide, chloroform, carbon tetrachloride, and turpentine. The mixtures were in all cases found to have a volume differing slightly from the sum of the volumes of the components, so that there is generally either a contraction or expansion in volume when two normal liquids are mixed. The author attributes this behaviour on the one hand to specific actions between the molecules of the liquids mixed, and on the other hand to the reduction of the internal pressure which attends the dilution of one liquid by another. H. C.

Compressibility Coefficients of the C_nH_{2n+2} Hydrocarbons. By Adolfo Bartoli (*Gazzetta*, 1896, **26**, i, 466—471).—The author has determined the compressibility coefficients K_t, at a temperature $t = 23°$, of a series of paraffinoid hydrocarbons obtained by fractionating Pennsylvanian petroleum, using a piezometer of the type described by Guillaume (*Études thermometriques*, p. 28). The results are given in the following table, together with the boiling-points, B, and the densities at 0°, d_0, of the hydrocarbons:—

	B	d_0	K_t	C	c	C/c
C_6H_{14}	68°	0·6950	0·0001592	0·5042	0·3719	1·355
C_7H_{16}	93	0·7328	0·0001341	0·4842	0·3776	1·282
C_8H_{18}	117	0·7463	0·0001214	0·5111	0·4084	1·251
C_9H_{20}	137	0·7624	0·0001125	0·5015	0·4003	1·252
$C_{10}H_{22}$	160	0·7711	0·0001054	0·5058	0·4065	1·244
$C_{11}H_{24}$	181	0·7817	0·0000974	0·5032	0·4069	1·236
$C_{12}H_{26}$	199	0·7915	0·0000917	0·5065	0·4102	1·234
$C_{13}H_{28}$	219	0·8017	0·0000874	0·4987	0·4039	1·233
$C_{14}H_{30}$	238	0·8130	0·0000827	0·4997	0·4090	1.221
$C_{15}H_{32}$	260	0·8224	0·0000787	0·4991	0·4099	1·217
$C_{16}H_{34}$	280	0·8287	0·0000754	0·4964	0·4142	1·198

W. J. P.

Capillary Behaviour of the Crystal Faces of Rock-salt and Sylvine towards the Mother Liquors. By St. Barent (*Zeits. Kryst. Min.*, 1896, **26**, 529—557).—Curie, Sohncke, Bravais, and others have shown theoretically that the particular forms occurring on a crystal are determined by the number of mass-points or molecules lying in unit area of the faces of those forms, which number is, in turn, intimately connected with the capillarity constant. The capillarity constant should be the same in all faces of the same form, but different for faces of different forms; the form the faces of which are most thickly studded with mass-points should be that developed

most frequently during the crystallisation of any particular substance, and should have a smaller capillarity constant than any other possible form on the crystal. The capillarity, measured between a crystal face and the mother liquor surrounding it, is, however, not conditioned solely by the crystalline structure but also by the nature of the mother liquor, the temperature, pressure, &c.; the different habits of the crystals of a substance which can be developed by crystallisation from different solvents and at different temperatures are thus due to changes in capillarity.

These apparently sound views not having yet been put to adequate experimental test, the author has made series of capillarity determinations with differently orientated plates of rock-salt and sylvine; the determinations made by Quincke's method of measuring the bordering angle (Randwinkel) between liquid and solid are in concordance with the theory.

The experiments made with rock-salt and its saturated aqueous solution show that crystallographically different crystal faces have a different capillary behaviour towards the same mother liquor; the mother liquor makes a smaller bordering angle with a crystalline face, the more thickly the latter is studded with mass-points. The bordering angles are, for rock-salt and its saturated aqueous solution, of the order 7·5° for the form {100}, 8·7° for {110}, 13·5° for {111}, and 11·1° for {210}, but on adding carbamide to the saturated mother liquor, the bordering angle on the form {100} increases, whilst that on {111} decreases, so that the latter angle becomes less than the former when the mother liquor contains a certain percentage of carbamide; the reason is thus given of the well-known curious fact, that whilst sodium chloride crystallises in cubes from a pure aqueou solution, it separates in octahedra from urine or an aqueous solution containing carbamide. The addition of caustic soda, chromic chloride, or potassium hydrogen oxalate to sodium chloride solution also causes the crystals formed to become octahedra, and in each of these cases the author finds that the bordering angle on the octahedron is less than that on the cube form. The addition of sodium carbonate, which does not alter the forms present of the sodium chloride crystals, was found not to reverse the order of magnitude of the bordering angles on the forms {100} and {111}. W. J. P.

Coefficients of Division of Phosphoric Acid between Ether and Water. By MARCELLIN BERTHELOT and GUSTAVE ANDRÉ (*Compt. rend.*, 1896, **123**, 344—349).—Ether free from alcohol and saturated with water was shaken with definite volumes of phosphoric acid solutions of various strengths, and the quantity of phosphoric acid in the ether and water respectively was determined by titration. With a solution of phosphoric acid in about 11 times its weight of water, it was found that 1 c.c. of water contained 0·0886 gram of phosphoric acid, whilst 1 c.c. of ether contained only 0·000033 gram, the coefficient of division being $\frac{1}{2700}$. With acid five times more concentrated, the coefficient was $\frac{1}{2900}$, whilst with a solution containing 0·434 gram of phosphoric acid per c.c. the quantity dissolved by the ether was infinitesimal. On the other hand, when ether containing a considerable quantity of phosphoric acid is agitated with an equal volume of

water, the latter removes practically all the acid just as in the case of sulphuric and hydrochloric acids.

When a very highly concentrated liquid phosphoric acid is agitated with ether, the two mix completely with large development of heat, and ether may be added in any proportion without causing any precipitation. If a small quantity of water is added, it mixes completely, but if the addition of water is continued, there at last comes a point when a small quantity of ether separates, highly charged with phosphoric acid. The addition of more water causes the separation of a larger volume of ether containing a lower proportion of acid, and still more water separates a still larger volume of ether containing still less acid, and this change continues as the addition of water is continued, until the coefficient already stated is reached. These highly concentrated liquids cannot, however, be regarded as simple aqueous solutions of phosphoric acid; they are really complex liquids containing water, phosphoric acid, and a compound of phosphoric acid and ether. Quantitative details of the experiments are given. C. H. B.

Degree of Dissociation of Electrolytes at 0°. By MEJER WILDERMANN (*Phil. Mag.*, 1896 [5], **42**, 102—103).—The author points out that Wood has wrongly attributed certain molecular freezing point depressions to him, and that, contrary to Wood's statement, in the paper cited Arrhenius's generalisation finds an excellent confirmation. H. C.

Influence of the Temperature of the Cold Jacket on Cryoscopic Measurements. By FRANÇOIS M. RAOULT. (*Zeits. physikal. Chem.*, 1896, **20**, 601—604.)—The observed freezing point is that temperature at which the velocity of cooling by radiation is equal to the velocity of heating by ice-formation. The latter velocity is proportional to the difference between the observed and true freezing point, that is, $t_0 - t_1$, hence also the velocity of cooling is so proportional, namely, $v = k(t_0 - t_1)$ or $(t_0 - t_1) = v/k$, a result similar to that of Nernst and Abegg. (Abstr., 1895, ii, 155). The true freezing point can, however, be readily found by observing the apparent freezing point at two or three different temperatures of the cold jacket, other conditions being similar. The values of v (the velocity of cooling) are taken for abscissæ and the observed freezing points, t_1, as ordinates and the curve (a straight line) produced to the value $v = 0$. The author finds that with solutions of the same substance at various concentrations, the difference $t_0 - t_1$ is proportional to the concentration, consequently to the depression, hence if C_0 and C_1 are the true and apparent depressions $t_0 - t_1 = qC_0$ and $C_1 - C_0 = t_0 - t_1$ hence $C_1 = C_0(1 + q)$ so that laws deduced for C_0 hold also for C_1 since q is a constant dependent only on the nature of the dissolved substance. In the author's experiments, q had the following values: pure water, $-0{\cdot}001$; sulphuric acid, $0{\cdot}004$; hydrogen chloride, $0{\cdot}002$; cane sugar. $0{\cdot}002$; alcohol, $0{\cdot}005$. It follows therefore that the temperature of the bath does not invalidate laws deduced from the freezing point depressions of various solutions of the same compound and also that the effect is very slight and does not noticeably affect the actual values of molecular depressions of different compounds, or the deduced laws, and further the effect can be readily allowed for and corrected. L. M. J.

NOTE BY ABSTRACTOR.—The above expression is deduced in a manner closely analogous to that employed by Wildermann (Abstr., 1896, ii, 291) with which it entirely agrees if the value $k(ts - t_1)$ is substituted for $v(ts = \text{convergence temperature})$.

Parabromotoluene as a Solvent in Cryoscopic Researches.—By EMANUELE PATERNÒ (*Gazzetta*, 1896, **26**, ii., 1—9).—The author has studied the possibility of using parabromotoluene as a solvent in cryoscopic determinations; the molecular depressions of the freezing point of parabromotoluene melting at 26·88° by benzene, toluene, ethylenic bromide, ethylsuccinimide, ethylic oxalate, veratrole, thiophen, aniline, pyridine, ethylic alcohol, acetic acid, phenol, paracresol, and thymol were determined, and from the results it is concluded that the value 82·20 calculated by van't Hoff's formula from the latent heat of fusion is the normal value of this constant.

Parabromotoluene behaves in cryoscopy similarly to the hydrocarbons and their halogen and nitro-derivatives, giving normal results with neutral substances and bases, but only about half the normal molecular depressions with acids; with alcohols and phenols, the molecular depressions are practically normal in very dilute solutions, but, as the concentration is increased, the molecular depressions decrease rapidly with alcohols, and less rapidly with phenols.

Since parabromotoluene is easily purified, little liable to change, and does not exhibit superfusion, it should constitute a valuable solvent in cryoscopy. W. J. P.

Veratrole as a Solvent in Cryoscopic Researches.—BY EMANUELE PATERNÒ. (*Gazzetta*, 1896, **26**, ii, 9—16).—Cryoscopic determinations of benzene, paraxylene, bromotoluene, thiophen, aniline, pyridine, ethylic alcohol, glycerol diethylic ether, benzylic alcohol, phenol, thymol, acetic acid, and valeric acid in veratrole solution give 64 as the mean molecular depression of the freezing point of this solvent. Veratrole is not cryoscopically analogous in behaviour to the hydrocarbons or their halogen or nitro-derivatives but gives almost the same molecular depressions of the freezing point with substances of very varied types; with aniline, phenol and thymol the molecular depressions are extraordinarily constant with change of concentration. The cryoscopic behaviour of veratrole is in many respects similar to that of benzophenone. W. J. P.

Nitrobenzene as a Solvent in Cryoscopic Research.—By G. AMPOLA and E. CARLINFANTI (*Gazzetta*, 1896, **26**, ii, 76—91).—From determinations of the depression of the freezing point of nitrobenzene by benzene, bromobenzene, toluene, bromotoluene, paraxylene, benzaldehyde, veratrole, naphthalene, ethylic oxalate, thiophen, chloroform, bromoform, formic acid, acetic acid, valeric acid, isobutyric acid, ethylic alcohol, isopropylic alcohol, isobutylic alcohol, caprylic alcohol, trimethylcarbinol, benzylic alcohol, cinnamic acid, glycerol ethylic ether, phenol, thymol, paracresol, aniline, dimethylaniline, coniine, quinoline, pyridine, and piperidine, the authors find the molecular depression to be 69, the number calculated by van't Hoff's formula being

68·6. The determinations indicate that the behaviour of nitrobenzene as a solvent is analogous to that of benzene, bromoform, paraxylene and parabromotoluene. Paraxylene, benzene, toluene, veratrole, naphthalene, bromoform, chloroform, bromobenzene, bromotoluene, ethylic bromide and benzaldehyde give normal depressions, as does also thiophen, although it behaves abnormally in benzene solution. Aniline and dimethylaniline give very constant molecular depressions between very wide limits of concentration; quinoline is also nearly normal in behaviour, and the irregularities noted with the other bases examined is certainly due to reaction occurring between the dissolved substance and the solvent. The behaviour of acids, alcohols and phenols is strictly analogous to their behaviour in benzene, paraxylene and bromoform. W. J. P.

Behaviour of Phenol as a Solvent in Cryoscopy. By EMANUELE PATERNÒ (*Gazzetta*, 1896, **26**, ii, 363—374).—The author has made series of determinations of the molecular depression of the freezing point of phenol by water, bromoform, toluene, paraxylene, nitrobenzene, parabromotoluene, veratrole, ethylic oxalate, alcohol, benzylic alcohol, glycerol diethylic ether, thymol, methylic salicylate, formic acid, acetic acid, valeric acid, pyridine, aniline, dimethylaniline, and ethylsuccinimide. The molecular depressions of the freezing point by bromoform, nitrobenzene, toluene, parabromotoluene, and paraxylene diminish gradually as the concentration increases; this behaviour is different from that observed with other hydrocarbons and their halogen derivatives by Eijkman (Abstr., 1890, 324) who found that the molecular depressions tended to increase with the concentration. The alcohols and phenols behave very regularly and the molecular depressions are very constant between wide limits of concentration; with the diethylic ether of glycerol, which is a secondary alcohol, the molecular depression is not nearly so constant. The tendency of the molecular depression to increase with the concentration, noticed by Eijkman with phenolic substances in phenol solution, is not confirmed by the author; the molecular depressions caused by thymol and methylic salicylate gradually decrease as the concentration increases, and Garelli and Montanari have observed similar behaviour in the case of the dihydroxybenzenes. The molecular depression caused by acids is small, even in dilute solutions, and it decreases considerably as the concentration increases: this result agrees with that obtained by Eijkman. The rate of increase of the molecular depression with concentration caused by pyridine, aniline, and dimethylaniline is not so great as in the case of the alkaloids studied by Eijkman; the molecular depression for ethylsuccinimide, however, increases rapidly with the concentration. Veratrole and ethylic oxalate give high molecular depressions which also increase with the concentration. Water in dilute solutions gives a low molecular depression which rapidly increases with the concentration; this substance behaves, therefore, similarly to the acids.

Phenol seems to differ in behaviour from other solvents used in cryoscopic work, in that there is a general tendency for the molecular

depressions to increase with the concentration, whilst in general the molecular depression decreases as the concentration increases
W. J. P.

The Cryoscopic Behaviour of Substances similar in Composition to the Solvent. By FELICE GARELLI (*Gazetta*, 1896, **26**, ii, 380–387).—Cryoscopic determinations show that cyclopentadiene (Abstr., 1896, i, 289), as would be expected from the author's previous results (*ibid*, ii, 292), forms solid solutions with freezing benzene but behaves quite normally in paraxylene solution. Dicyclopentadiene, however, behaves quite normally in freezing benzene, phenanthrene naphthalene, and diphenyl.

Fluorene gives normal results in benzene and naphthalene solution, but the addition of fluorene to phenanthrene raises the freezing point of the latter, owing to the formation of a solid solution. W. J. P.

Osmotic pressure of Ether and Chloroform in the Nerve Cells. By HEINRICH DRESER. (*Zeits. physikal. Chem.*, 1896, **21**, 108—112)—The best narcotising mixture in the case of chloroform is 10 grams in 100 litres of air, in the case of ether 20 grams in the same volume. Assuming that the protoplasmic solution is in equilibrium with this mixture, the author calculates the osmotic pressure of the two compounds in their solution, the results being 982·4 atmospheres and 703·6 atmospheres for the chloroform and ether respectively. L. M. J.

Labile Equilibrium of Salt Solutions. By ADOLF BLÜMCKE (*Zeits. physikal. Chem.*, 1896, **20**, 586—592).—Contains thermodynamical diagrams representing states of labile equilibrium of salt solutions. (Abstr. 1893, ii, 447). L. M. J.

Hypothesis of the Coloration of Ions. By GAETANO MAGNANINI (*Gazzetta*, 1896, **26**, ii, 92—96. Compare Magnanini and Bentivoglio, Abstr., 1894, ii, 129).—Determinations of the electrical conductivity of dimethylvioluric acid give $K = 0{\cdot}00157$ and $\mu\infty = 352$; the potassium salt is much more highly dissociated in solution and $V = 1280$, $\mu = 96{\cdot}3$. Solutions of the acid, in accordance with Ostwald's hypothesis of the coloration of the ions, are less strongly coloured than those of the salt.

With solutions of isonitrosodiketohydrindene, the values $K = 0{\cdot}0000105$ and $\mu\infty = 355$ were obtained; the yellow colour of the solid substance persists in solution, but highly dilute solutions are of a more reddish tint.

Diethylic dichloroquinonedimalonate (Grindley and Jackson, Abstr., 1893, i, 312) is yellow in the solid state, and nearly insoluble in water; when heated with water, a small quantity dissolves, and the solution becomes blue, whilst on cooling the substance crystallises out, the solution becoming colourless and having a much smaller electrical conductivity when cold than when hot. On adding a trace of acid, the salt dissolves and the solution becomes deep blue. W. J. P.

Transparency of Solutions of Colourless Salts. By WALTHÈRE

SPRING (*Zeits. anorg. Chem.*, 1896, **13**, 19—28).—Solutions of various strengths of the following carefully purified salts were examined: lithium chloride, sodium chloride and nitrate, potassium bromide, chloride and nitrate, and the chlorides of magnesium, calcium, strontium, and barium. The relative amount of light absorbed by a column of each salt solution is determined by comparing it with an equal column of water, using glass plates to equalise the transparency of the two columns. The relative absorption of the salt solutions compared with water is then calculated from the equation $J_2 = J_1 C^{a(n_1 - n_2)}$ when a = the absorption of one glass plate, n = the number of plates used, and J_1 = the intensity of the light after passing through the water.

The results obtained show that the colour of a column of water is not altered by the presence of dissolved salts, and all the salt solutions gave the same spectrum as pure water. The transparency of the solution depends on the nature of the dissolved salt and on the concentration: it increases as the concentration decreases, but is not proportional to the concentration. The absorption of a salt solution does not equal the sum of the absorptions of the solvent and the dissolved salt. E. C. R.

Autocatalysis. By F. G. DONNAN (*Ber.*, 1896, **29**, 2422—2423).—The equation $dx/dt = km\,(a - x)^2$, which Goldschmidt has shown (Abstr., 1896, ii, 638) to express the velocity of etherification in alcoholic solution, is identical, since m is constant, with the equation $dx/dt = km^2\,(a - x)^2$ which should express the velocity of etherification if no autocatalysis occurs: if the hydrogen ions acted catalytically according to a linear law, the equation $dx/dt = k_1\,m^3\,(a - x)^3$ should hold. The author therefore concludes that no autocatalysis occurs during direct etherification. The fact that etherification is a bimolecular reaction, as Goldschmidt finds, is a necessary consequence of the electrolytic dissociation and is in itself proof of the non-occurrence of autocatalysis; etherification is a similar reaction to the formation of carbamide from ammonium cyanate (Walker and Hambly, *Trans.*, 1895, 746). W. J. P.

Velocity of Decomposition of some Sulphur and Phosphorus Compounds by Water. By GIACOMO CARRARA and I. ZOPPELARI (*Gazzetta*, 1896, **26**, i, 483—493). In continuation of their previous work (Abstr., 1894, ii, 412), the authors have determined the velocity of reaction in non-homogeneous systems consisting of water and the compounds named in the appended table, using for calculation the formula

$$\frac{1}{t\,O} \log \frac{A}{A - x} = AC,$$

in which O is the surface area of the two liquids in contact, A the quantity of decomposable liquid, x the quantity of the latter decomposed during the time t, and C is a constant. The sp. gr. d of the liquids at 11°/4°, and the temperature T at which the experiments were made are also given; both AC and x/t are calculated.

The quantity AC deduced from the logarithmic formula is in all

cases more constant than the ratio x/t, thus confirming the authors view that the logarithmic expression should be used in non-homogeneous systems.

Substance	d	T	A	AC	$\frac{x}{t}$
$SOCl_2$	1·6577	1°	1	0·0152	0·0317
$S_2O_5Cl_2$	1·8512	10	1	0·00331	0·00571
,,	,,	30	1	0 0100	0·0160
PCl_3	1·5941	5	1	0·000297	0·0071
PBr_3	2·9132	5	10	0·0111	0·0239
,,	,,	10	10	0·0212	0·0442
$POCl_3$	1·6529	5	10	0·000348	0·0782
,,	,,	10	10	0·00067	0·0138
$PSCl_3$	1·6531	10	10	0·000132	0·000289
,,	,,	30	10	0·000238	0·00041

W. J. P.

Velocity of Formation of Alkali Xanthogenates [Alkali Ethylic $\alpha\beta$ - dithiocarbonates]. By NATALE VIANELLO MORO. (*Gazzetta*, 1896, **26**, i, 494—501).—If a satisfactory inactive solvent could be found, the formation of an alkali xanthogenate [ethylic $\alpha\beta$-dithiocarbonate] in accordance with the equation $CS_2 + KHO + EtOH = CS_2OEtK + H_2O$, would constitute a reaction of the third order, and might then be advantageously studied, because the velocities of very few such reactions have been determined. Since such a solvent could not be found, the reaction was examined in alcoholic solution, and, as was to be expected, then proceeded as a reaction of the second order, the quantity of alcohol present being a constant. W. J. P.

Hydrolysis of Ferric Chloride. By H. M. GOODWIN (*Zeits. physikal. Chem.*, 1896, **21**, 1—15).—When a neutral solution of ferric chloride is considerably diluted, the solution, although colourless at first, soon becomes yellow, whilst also the molecular conductivity increases with the time since dilution. The author finds the velocity of the change of conductivity increases with the dilution, and that the change does not commence until some time after dilution, this time increasing with the concentration. The time required to reach a final state of equilibrium is also very variable, being 3 hours for 0·0001 N, and a week for 0·0006 N. The velocity of the change, when once started, rapidly increases, reaches a maximum, and then decreases. The author considers that these anomalies are due to the hydrolysis of the ferric chloride on dilution, in accordance with the equation $FeCl_3 + H_2O = FeOH'' + H' + 3Cl'$, in which case an increase in conductivity is caused by the greater velocity of the new ions. The slow after increase is caused by the further hydrolysis and formation of the colloïdal hydroxide. Conductivity and cryoscopic measurements yield numbers which are in accord with this view, but not with the view that hydrolysis to $Fe(OH)_3$ occurs immediately after dilution.

L. M. J.

Velocity of the reaction between Ferric Chloride and Stannous Chloride. By ARTHUR A. NOYES (*Zeits. physikal. Chem.*, 1896, 21, 16.)—The author's opinion that the reaction between ferric chloride and stannous chloride is one of the third order is contrary to that of Kortright, who considered that, if hydrolysis of the ferric chloride to ferric hydroxide is allowed for, the reaction is of the second order (Abstr., 1895, ii, 159 and 257). The results obtained by Goodwin (preceding abstract) show that hydrolysis to ferric hydroxide can occur only to a very small extent, so that Kortright's explanation cannot hold. L. M. J.

Explosions. By C. HOITSEMA (*Zeits. physikal. Chem.*, 1896, 21, 137—148).—The first explosive decomposition studied was that of silver oxalate, $Ag_2C_2O_4 = Ag_2 + 2CO_2 (= 29500$ Cal.). Preliminary experiments proved that the same products were obtained during slow decomposition. The velocity constant was found to increase with the temperature, the curve bending upwards very rapidly at about 165°. When the reaction velocity was then carefully determined at fixed temperatures, satisfactory constancy was found, the mean results for 150°, 155°, 160° and 170° being respectively 0·00292, 0·00481, 0·00711 and 0·0174, values which satisfactorily obey Nernst's expression $\log k = -A/T + c$. Sulphide of nitrogen was qualitatively examined, and was found to give the same products whether the decomposition was slow or rapid. The velocity was found further to increase with the temperature. Mercury and silver fulminates were also examined, but in this case the products of decomposition depend on the velocity of decomposition and no quantitative measurements were made. L. M. J.

The Theory of "Corresponding" States. By G. BAKKER (*Zeits. physikal. Chem.*, 1896, 21, 127—133).—The author deduces the following conclusions respecting compounds obeying Van der Waals' laws, at "corresponding" states. (1) The deviations from the laws of Joule, Boyle, and Gay Lussac are equal. (2) The change in the molecular entropy by vaporisation is equal for all compounds. (3) The molecular entropy is equal. (4) The specific heat is inversely proportional to the molecular weight. (5) The molecular energy and the molecular free energy are proportional to the critical temperature. (6) The velocity of sound is directly proportional to the critical temperature and inversely proportional to the molecular weight.

L. M. J.

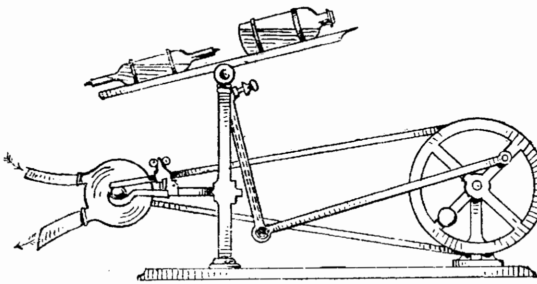
Isomorphism XII. By JAN W. RETGERS (*Zeits. physikal. Chem.* 1896, 20, 481—546).—Beryllium is frequently regarded as isomorphous with the elements of the zinc group, chiefly owing to the form resemblance of some of its mineral compounds to those of zinc, and tothe alleged isomorphous mixtures of beryllium sulphate with the vitriols (Klatzo, *J. pr. Chem.*, 1869, 106, 227). The minerals helvite and danalite, in which mixtures of silicates and sulphides of beryllium manganese, iron and zinc are found, are composed of the silicate of the former combined with the isomorphous mixture of the other

silicate and the sulphides, that is, $3Be_2SiO_4,3(MnFe)SiO_4,2(MnFe)S$ represents helvite. Similar remarks apply to other beryllium minerals which are shown to contain no isomorphous mixtures of beryllium silicate with the silicates of the zinc group. The author endeavoured to prepare mixed crystals of beryllium sulphate with the sulphates of copper, nickel, iron and manganese, but although several solutions were in each case crystallised no trace of mixed crystals was obtained, a result completely at variance with the results of Klatzo, but agreeing with those of Marignac. From this, the author concludes that beryllium salts are not isomorphous with the salts of the metals of the magnesium group. The author adds other examples of the use of etched-figures (Abstr., 1895, ii, 309) in the determination of isomorphism. In all the cases hitherto examined, isomorphous compounds show similar etched-figures when subjected to the same reagent, but the converse does not necessarily hold, so that although rutile, zircon, and tinstone give similar figures with hydrogen potassium fluoride, the author does not consider them isomorphous, while the isomorphism also of silicon and titanium compounds is doubtful. This method is also useful in examining cases of hemimorphism, and cases are recorded where supposed hemihedral compounds are proved to be holohedral, as, for instance, copper oxide, and phosgenite [cromfordite].

Cases of anomalous mixtures are next considered. Many salts in crystallising absorb organic colouring matters, and frequently such mixtures have a more or less fibrous structure; probably the origin of many fibrous minerals is due to a similar cause. The colour also of various minerals may be due to organic mixtures, as, for example, yellow blende (free from iron), topaz, amethyst, rose quartz, &c. Some minerals also form anomalous mixtures with others, thus the oxides of tin and titanium form crystals coloured by ferric, chromic or manganic oxides. The cause of this is not clear but it may be due to a crystallographic opposition, the axes of one being parallel to the interaxes of the second. Numerous examples of other anomalous mixtures are recorded. L. M. J.

Isomorphism of Alkali Salts. By R. KRICKMEYER (*Zeits. physikal. Chem.*, 1896, **21**, 53—89). The specific gravity of isomorphous mixtures is stated by Retgers to be a purely additive function, and the experiments of the author on the specific gravities of isomorphous mixtures of potassium and ammonium salts verify this conclusion, hence the sp. gr. of crystals is used as a test for mixtures. Such mixtures were obtained in the case of the potassium and ammonium alums, the monoclinic double sulphates with zinc, nickel, &c., and the chlorides. With the phosphates and tartrates, however, the miscibility of the salts was very slight. In the case of sodium and potassium salts no mixed crystals could be obtained although the alums, double sulphates with zinc, &c., chlorides, and bromides were investigated. Sodium and ammonium chlorides, lithium and sodium chlorides and sulphates, lithium and potassium chlorides and sulphates, were also examined but in no case could mixed crystals be obtained, so that the only truly isomorphous compounds are those of potassium and ammonium. The paper contains a number of carefully determined specific gravities of the salts examined. L. M. J.

A New Shaking Apparatus for the Laboratory. By MAX VON RECKLINGHAUSEN (*Ber.*, 1896, **29**, 2372—2373).—The apparatus is represented in the diagram one-tenth its natural size. Its advantages



are (1) That friction is reduced to a minimum. (2) That the different parts are not corroded by the air of the laboratory. (3) That only a small force is needed to set the apparatus in motion. The platform consists of an iron frame covered with coarse wire gauze, to which the flasks, &c., to be shaken can easily be strapped. J. J. S.

Inorganic Chemistry.

Does Hydrogen find its Proper Place at the Head of Group I. or at the Head of Group VII.? By ORME MASSON (*Chem. News*, 1896, **72**, 283—284).—As reasons for assigning a position to hydrogen at the head of Group VII. in the periodic system, the author points to its monad valency, its diatomic molecule, its gaseous character and extremely low boiling-point. The atomic weight of hydrogen places it rather in Group VII. than in Group I., and arguments based on substitution cut both ways, as an inorganic chemist would be most struck with the analogy between hydrogen and the alkali metals, an organic chemist with the analogy between hydrogen and the members of the chlorine group.

JOHN A. R. NEWLANDS (*ibid.*, 1896, **72**, 305) points out that in 1872 he classed hydrogen and chlorine together on account of their mutual replaceability, and because the atomic weight of hydrogen indicates that it is really the lowest member of the chlorine group.

H. C.

Slow Oxidation of Hydrogen and of Carbonic Oxide. By VICTOR MEYER and MAX VON RECKLINGHAUSEN (*Ber.*, 1896, **29**, 2549—2560).—It is known that hydrogen is slowly oxidised, when led through a solution of potassium permanganate, and a repetition of this experiment showed that the gas if left over an alkaline or neutral solution of the salt slowly decreased in volume until all had been absorbed. Carbonic oxide behaved similarly.

On shaking the mixture on the shaking-machine lately devised by von Recklinghausen, a similar result was arrived at; if, however, an acid solution of permanganate was employed, a large volume of gas remained unabsorbed, which on examination was found to be oxygen. 39 c.c. of hydrogen after shaking for 15 hours with 29 c.c. of an acid solution of permanganate yielded 17·8 and 20·4 c.c. of oxygen.

Since an acid solution of permanganate evolves oxygen by itself on standing, three experiments were conducted side by side, the hydrogen being replaced in one case by air and in the other by carbonic anhydride; the quantities obtained were, however, very different, the carbonic anhydride experiment yielding only 2·5 c.c. of oxygen, whilst with the hydrogen 19·1 c.c. was obtained. The amount of oxygen evolved does not increase after a certain limit has been reached, the same volume being obtained whether the mixtures were shaken for 17 or for 87 hours.

The quantity of oxygen evolved from an acid solution of permanganate on standing differs considerably from that given off on shaking. A closed tube completely filled with the solution burst after standing 2½ months in the dark, whilst one which had been filled one-third with permanganate and two-thirds with air was found to contain 50 c.c. of oxygen at the end of the same period, that is, nearly 20 times as much as was given off in the majority of the experiments when the liquid was shaken. It was further found that the temperature had a considerable influence on the amounts evolved.

The formation of oxygen in these experiments could be readily understood on the supposition that hydrogen peroxide was at first produced and that this subsequently reacted with the permanganate, evolving oxygen. Since, however, carbonic oxide behaves in a precisely similar way (yielding 14·5—11·5 c.c. of oxygen when 39·5 c.c. of the gas is shaken with 20 c.c. of permanganate solution for 23½ hours), this explanation does not hold good.

The evolution of oxygen is irregular, and the numbers obtained are merely approximate, the quantities evolved in two similar experiments seldom agreeing.

It might be supposed that the large quantity of oxygen evolved might be due to the diminution of pressure consequent on the absorption of the hydrogen; that this is not the case, however, was shown by shaking carbonic anhydride and air with permanganate under diminished pressure, the volume of oxygen given off (2—3 c.c.) remaining unaltered.

The authors hope to throw light on these phenomena by means of further experiments conducted on other reducing gases, such as the hydrocarbons, &c. Meanwhile, they consider that the most probable explanation is that put forward by van't Hoff in explanation of the simultaneous oxidation of triethylphosphine and indigo solution, namely, that in slow oxidations the oxygen molecule acts as two atoms (?) or ions (?). The reaction in this case proceeding thus

$$\begin{matrix} H_2 \\ H_2 \end{matrix} + \begin{matrix} OO \\ OO \end{matrix} = 2H_2O + O_2$$

the quantity of oxygen given off agreeing approximately with this equation. J. F. T.

Behaviour of Halogen Hydrides at Low Temperatures. By THADDAEUS ESTREICHER (*Zeits. physikal. Chem.*, 1896, **20**, 605—609).—The author has determined the boiling points and freezing points of hydrogen chloride, bromide, and iodide, as well as the critical temperatures of the last two compounds. The low temperatures were obtained by means of ethylene, and by carbonic anhydride and ether, and were measured by a helium thermometer. (Abstr., 1896, ii, 597). The results obtained were

	Pressure	b. p.	m. p.	Crit. temp.
Hydrogen chloride ...	745·2	−83·7°	−111·1°	—
Hydrogen bromide ..	738·2	−64·9°	− 87·9°	+ 91·3°
Hydrogen iodide......	739·8	−34·1°	− 50·8°	+150·7°

The liquid was in each case clear and colourless, and the solid an iron grey mass, but in the case of the iodine compounds the products were frequently coloured by dissolved iodine. L. M. J.

Crystallography of Iodates and Periodates. By ARTHUR S. EAKLE (*Zeit. Kryst. Min.*, 1896, **26**, 558—588).—The author has investigated the conditions of growth most favourable to the cultivation of well-developed crystals of a number of salts and determined their geometrical and optical properties.

Well-developed transparent hydrated crystals of the trigonal pyramidal sodium periodate, $NaIO_4 + 3H_2O$, can be obtained by very slow spontaneous evaporation of the pure aqueous solution, but in a much shorter time from solutions containing sodium nitrate; $a : c = 1 : 1·0942$. The crystals deposited from a pure aqueous solution consist of dextrogyrate and lævogyrate individuals in approximately equal numbers, but in solutions containing sodium nitrate the remarkable fact is observed that the lævogyrate crystals outnumber the dextrogyrate ones by about four to one. The anhydrous ditetragonal dipyramidal crystals of sodium periodate, $NaIO_4$, deposited from aqueous solution at above 30° have the axial ratio $a : c = 1 : 1·5900$.

Aqueous solutions of ammonium periodate containing ammonia deposit, on spontaneous evaporation, trigonal rhombohedral crystals having the composition $(NH_4)_4I_2O_9,3H_2O$, and the axial ratio $a : c = 1 : 1·6118$; when the solution during evaporation has lost nearly all its free ammonia, crystals of the normal periodate, NH_4IO_4, isomorphous with those of anhydrous sodium periodate, separate; $a : c = 1 : 1·5228$. Aluminium periodate, $Al(IO_4)_3 + 3H_2O$, crystallises in holohedral cubic forms from a solution containing nitric acid.

Rhombic bipyramidal crystals of anhydrous sodium iodate, $NaIO_3$, are deposited from an aqueous solution at 100°; $a : b : c = 0·9046 : 1 : 1·2815$; at lower temperatures, long needles of the hydrated salt are

deposited. Ammonium iodate, NH_4IO_3, crystallises in long prisms; $a : b : c = 0·9948 : 1 : 1·4335$. Silver iodate, $AgIO_3$, in thin, colourless, transparent plates of adamantine lustre from solutions containing ammonia; $a : b : c = 0·8832 : 1 : 1·3072$. These three salts are isomorphous.

Potassium iodate is cubic and holohedral, but the habit of the crystals varies widely with changes in the temperature of crystallisation; the crystals are isomorphous with those of rubidium iodate, which consist of opaque, white cubes.

Calcium iodate, $Ca(IO_3)_2 + 6H_2O$, separates from an aqueous or nitric acid solution in rhombic prisms; $a : b : c = 0·4357 : 1 : 0·5231$. If, however, the solution contains a small quantity of calcium chromate, a second form of calcium iodate having the same composition, is deposited; the new crystals are rhombic pyramidal prisms; $a : b : c = 0·64652 : 1 : 0·27682$. Calcium iodate is thus dimorphous.

The double compound of sodium iodate and iodide, $2NaIO_3$, $3NaI_1 + 20H_2O$, crystallises in dihexgonal bipyramidal prisms; $a : c = 1 : 2·1892$. Rubidium nitrate crystallises in ditrigonal scalenohedral prisms; $a : c = 1 : 1·2360$.

The crystallographic properties of the rhombic aluminium nitrate, $Al(NO_3)_3 + 9H_2O$, the monoclinic barium chlorate, $Ba(ClO_3)_2 + H_2O$, and the rhombic barium permanganate, $BaMn_2O_8$, were also determined.

W. J. P.

Reduction of Sulphuric Acid by Copper, as a Function of the Temperature. By LAUNCELOT W. ANDREWS (*J. Amer. Chem. Soc.*, 1896, **18**, 251—254).—By means of suitable apparatus, the author has been able to show—(1) That sulphuric acid (98·4 per cent.) begins to appreciably dissociate at a temperature somewhat below 70°, probably 67°; (2) That sulphuric acid in the presence of air or oxygen will dissolve copper at the ordinary temperature, without the evolution of a trace of sulphurous anhydride; (3) That the reduction of sulphuric acid by copper does not begin below 86°, that is, not until the acid has become partly dissociated into anhydride and water. Baskerville's statement (Abstr., 1896, ii, 474) that sulphuric acid is reduced by copper at 0° is therefore incorrect.

J. J. S.

Free Hydrazine. By CORNELIS A. LOBRY DE BRUYN (*Rec. Trav. Chim.*, 1896, **15**, 174—184; Compare Abstr., 1895, ii, 347).—Free hydrazine is best prepared by the action of barium oxide on hydrazine hydrate. The hydrate is added in small quantities at a time to the barium oxide contained in a flask, which is cooled from time to time and should be provided with a neck some 50 cm. long, bent at right angles at its upper end so that it can be directly attached to the condenser. The flask is first heated for several hours in a glycerol bath at 110—120°, and the contents are then distilled under a pressure of 150—100 mm. To prevent oxidation, the apparatus is filled with dry hydrogen. The base, which is collected in a cooled receiver, still contains 3—4 per cent. of water, and is, therefore, again distilled in a smaller flask, with a little barium oxide, the apparatus again being filled with dry hydrogen.

The free base melts at 1·4°; it can, however, be cooled several degrees below this before it freezes. Its boiling points, determined in an atmosphere of dry hydrogen, are 56° at 71 mm., 113·5° at 761·5 mm., and 134·6° at 1490 mm. pressure. Its sp. gr. = 1·014 at 15°/15°, that is, almost the same as that of the hydrate.

The refractive index, as determined by Eijkman, is given as

	$n\beta$	$n\alpha$	A	$\beta - \alpha$
	1·47988	1·46953	1·45693	0·01035
Gladstone's formula..	15·18	14·86	14·46	0·33
Lorentz's formula ...	8·99	8·82	8·62	0·17

d = 1·0114 t = 17·8° MV = 31·64.

Calculated for the group NH_2, the dispersion = 0·16 according to Gladstone's formula and 0·09 according to Lorentz. These numbers are practically the same as those calculated from pentamethylenediamine (*Rec. Trav. Chim.*, 1893, **12**, 281).

As regards its solubility, hydrazine resembles both water and hydroxylamine; it is miscible in all proportions with methylic, ethylic, propylic, isobutylic, and amylic alcohols, but is only very sparingly soluble in other organic solvents. Many salts dissolve in it, and determinations of their solubilities are given.

Hydrazine apparently combines with sodium chloride, as a considerable amount of heat is developed on mixing the two and the whole sets to a crystalline mass on cooling. Ammonium salts are decomposed by the base, and lead nitrate is dissolved by it. The base itself may be heated to 300—350° without undergoing perceptible decomposition; even after heating for an hour at the boiling point of sulphur part of it remains unaltered.

The critical temperature, as determined in Altschul's apparatus (*Zeits. physikal. Chem.*, 1893, **11**, 582) is 380°. According to Boltwood, stability of the base at high temperatures depends on the pressure. The decomposition first proceeds according to the equation

$$2N_2H_4 = N_2 + H_2 + 2NH_3,$$

but the final decomposition is $3N_2H_4 = N_2 + 4NH_3$.

The base is a strong reducing agent, it readily bursts into flame in chlorine; bromine and iodine also react violently. It is slowly oxidised by dry air free from carbonic anhydride, and also by oxygen; in the latter case, the temperature gradually rises to 100°, and ammonia can readily be recognised. Yellow phosphorus also acts on an aqueous solution of the base, forming, probably, hydrides of phosphorus.

Sodium reacts with the base suspended in dry light petroleum, yielding hydrogen, ammonia, and a brown solid substance.

J. J. S.

Oxidation by means of Hydroxylamine. By FRITZ HABER (*Ber.*, 1896, **29**, 2444—2445).—Hydroxylamine readily converts

ferrous hydroxide into the ferric compound, and may be recognised by this reaction, which is not given by hydrazine. The hydroxylamine is almost completely converted into ammonia.

An interesting lecture experiment to illustrate the double function of hydroxylamine as an oxidising and reducing agent may be carried out by adding hydroxylamine hydrochloride to a hot emulsion of ferrous hydroxide precipitated by means of caustic soda. The greenish mass rapidly becomes reddish brown, owing to the oxidation of the hydroxide. If now the liquid be acidified and a fresh quantity of hydroxylamine hydrochloride added, the latter acts as a reducing agent, and rapidly converts the ferric into a ferrous salt, the change being rendered evident by the disappearance of the yellow colour.

A. H.

Nitrohydroxylamine. By ANGELO ANGELI (*Gazzetta*, 1896, **26**, ii, 17—25).—On treating hydroxylamine with acidic chlorides or anhydrides, or with an alkylic salt of an organic acid in alkaline solution, derivatives having the constitution R·CO·NH·OH or OH·CR:N·OH are obtained. It seemed of interest to endeavour to prepare a substituted hydroxylamine, in which the acidic group was an inorganic acidic radicle. With this object, a cold saturated solution of hydroxylamine hydrochloride (1 mol.) is poured into a concentrated alcoholic solution of sodium ethoxide (3 mols.), and to this, after filtration, ethylic nitrate (1 mol.) is added; a white precipitate of *sodionitrohydroxylamine*, $Na_2N_2O_3$, separates immediately, but cannot be further purified because of its great solubility in water. On adding barium chloride to its dilute aqueous solution, a heavy, white, minutely crystalline precipitate of the corresponding *barium* salt, $BaN_2O_3 + H_2O$, is deposited; it loses its water at 115—120°.

On treating either the sodium or barium salt with a mineral acid, a violent evolution of nitric oxide occurs, almost quantitatively in accordance with the equation, $H_2N_2O_3 = H_2O + 2NO$; the salts also decompose on heating, giving nitric oxide, and leaving the metallic oxide. The aqueous solution of the sodium salt is readily decomposed by boiling, and nitrites and nitrates formed from the nitric oxide evolved are found in solution; the barium salt is not decomposed by prolonged boiling with water, and is much more stable in the air than the sodium salt.

The aqueous solution of the sodium salt gives a white precipitate with lead acetate or cadmium sulphate; a yellow solution, which rapidly deposits mercury, with mercuric chloride; a deep brown-red coloration, which disappears on boiling, with uranium nitrate; and a yellow precipitate, which rapidly blackens, with silver nitrate; it reduces Fehling's solution, and gives a violet to brown coloration with ferric chloride.

Mixtures of the sodium salt with sodium thiocyanate or hypophosphite, or with antimony trisulphide and sulphur or carbon, explode violently when struck; when mixed with red phosphorus, the sodium salt also detonates if struck, but the mixture is less sensible to shock than that of red phosphorus with potassium chlorate.

According to its method of formation, nitrohydroxylamine should have the constitution $NO_2 \cdot NH \cdot OH$; it might readily undergo intramolecular change and assume the constitution $OH \cdot N \colon NO \cdot OH$ or $\begin{matrix} HO \cdot N \\ HO \cdot N \end{matrix} > O$.

It is interesting to note that nitrohydroxylamine is the last missing member of the series of acids corresponding with the five oxides of nitrogen; it takes the vacant place between hyponitrous and nitrous acids in the series and corresponds with a hydrate of nitrogen dioxide. W. J. P.

The Electrolysis of solutions of Ammonia containing Salts and Bases. By SIMA M. LOSANITSCH and MILORAD Z. JOVITSCHITSCH (*Ber.*, 1896, **29**, 2436—2438). When a solution of ammonia and common salt is electrolysed in the usual Hofmann apparatus, there is always a deficiency in the nitrogen evolved. This is due to the occurrence of secondary reactions. When a chloride is present, the liquid is found to contain hypochlorite, which is either a direct product of the action of chlorine on the ammonia, or an indirect product formed by the action of water and ammonia on previously formed chloride of nitrogen. A loud explosion occurred when the graphite electrode was heated, and the authors ascribe this to the presence of chloride of nitrogen. When the formation of hypochlorite is prevented by heating the liquid, the correct ratio of nitrogen to hydrogen is obtained. When potassium bromide is used, a hypobromite is formed, and iodide of nitrogen and a hypoiodite when potassium iodide is employed. When caustic potash or potassium sulphate is added, as well as when ammonia itself in dilute solution is submitted to electrolysis, a nitrite is produced and the volume of nitrogen obtained is too small. A. H.

Hyponitrous Acid. By ARTHUR R. HANTZSCH and LUDWIG KAUFMANN (*Annalen*, 1896, **292**, 317—340. Compare Abstr., 1896, ii, 520).—Silver hyponitrite is prepared by reducing sodium nitrite with sodium amalgam in strongly alkaline solution, and after removal of hydroxylamine with mercuric oxide, adding silver nitrate to the solution acidified with nitric acid; treated in this way, 20 grams of nitrite yields 2—3 grams of silver salt, and the method compares favourably with Piloty's (Abstr., 1895, i, 556), which consists in hydrolysing benzosulphydroxamic acid with 40 per cent. aqueous potassium hydroxide.

Hyponitrous acid is obtained in the solid state by adding the silver salt to ethereal hydrogen chloride until silver chloride ceases to be formed; the filtered medium is then evaporated as rapidly as possible in the desiccator, when the acid crystallises in leaflets. It is deliquescent and dissolves readily in water and alcohol; it is only sparingly soluble in petroleum, but more readily in ether, chloroform, and benzene; the crystals, when wet with ether, do not rapidly undergo change, but the dry substance explodes spontaneously, even at $-6°$. Determinations of the molecular weight, effected by adding the silver

salt to water containing a known quantity of hydrogen chloride, yield results in accordance with the formula $H_2N_2O_2$. Titration of hyponitrous acid with alkali, using phenolphthaleïn as indicator, shows that the hydrogen sodium salt, like hydrogen sodium carbonate, is neutral towards this indicator; if the solution is kept for a time at the ordinary temperature, sodium hydroxide and nitrous oxide are formed. Solutions of pure hyponitrous acid do not immediately liberate iodine from potassium iodide, but the amount of the free halogen gradually increases with time; diphenylamine develops an intense blue coloration, and if ferrous sulphate is added to concentrated sulphuric acid mixed with silver hyponitrite, the brown ring characteristic of nitrous and nitric acids is produced.

Ammonium hyponitrite, $H_4N{\cdot}O{\cdot}N{:}N{\cdot}OH$, is obtained by passing dry ammonia gas into a cooled solution of the acid in ether; it melts and decomposes at 64—65°, and at the ordinary temperature is resolved spontaneously into ammonia, water, and nitrous oxide. The salt dissolves readily in water, the solution being alkaline, but the aqueous and alcoholic solutions leave no residue on evaporation; normal ammonium hyponitrite has not been obtained.

Benzylic hyponitrite, $CH_2Ph{\cdot}O{\cdot}N{:}N{\cdot}O{\cdot}CH_2Ph$, is obtained from benzylic iodide and silver hyponitrite in ether, and crystallises from light petroleum in leaflets; it melts and evolves nitrogen at 43—45°, and explodes at 60° when rapidly heated. The salt is volatile at the ordinary temperature.

It has been generally accepted that hyponitrous acid decomposes into nitrous acid and water, but it is now established that nitrous acid and ammonia are among the products of change; it is found that hyponitrous acid is most stable in alkaline, least stable in acid, solution, an aqueous solution occupying the mean position.

Determinations of the molecular conductivity of hyponitrous acid have been made, and the results show that it is very low in a freshly prepared solution, increasing, however, with the lapse of time; in the case of the sodium salt, it is higher, and gradually decreases with time. The conductivity constant shows that hyponitrous acid is very feebly acidic, being of the same order as carbonic acid, and it is interesting to notice that the value for nitramide is even lower than that for hyponitrous acid. M. O. F.

The Isomerism of Compounds $N_2O_2H_2$. By ARTHUR R. HANTZSCH (*Annalen*, 1896, **292**, 340—358).—This paper does not lend itself to condensation. An attempt is made to establish a stereoisomeric relationship between the two compounds of the formula $N_2O_2H_2$, nitramide and hyponitrous acid. The author claims to have refuted Bamberger's criticisms on his views regarding the structure of diazo-salts. M. O. F.

Nitrogen Pentasulphide. By WILHELM MUTHMANN and A. CLEVER (*Zeits. anorg. Chem.*, 1896, **13**, 200—208).—*Nitrogen pentasulphide*, N_2S_5, is obtained by heating nitrogen sulphide N_4S_4 (Abstr., 1896, ii, 298) with pure carbon bisulphide at 100° for two hours under a pressure of five atmospheres. A deep red solution is obtained

together with a yellowish-brown, amorphous precipitate; the filtrate is distilled until the greater part of the carbon bisulphide is separated, and the residue is allowed to evaporate at the ordinary temperature in a vacuum. The red oily product, consisting of a mixture of the pentasulphide with sulphur, is triturated with perfectly dry ether as quickly as possible, when the greater portion of the sulphur remains undissolved. The residual sulphur is crystallised out by means of a freezing mixture (– 25°) and the filtrate allowed to evaporate in dry air; finally, the last traces of ether are removed by allowing the product to remain over calcium chloride, and the residual red oil is filtered. If the product is pure and contains no sulphur, it crystallises from a well-cooled solution in ether in metallic tablets resembling iodine. A cryoscopic determination of the molecular weight, using benzene as the solvent, gave numbers agreeing with the formula N_2S_5. The amorphous bye-product mentioned above gave, on analysis, numbers agreeing with the formula $C_3N_3S_3$; it is a very finely divided yellow powder, is extremely hygroscopic and obstinately retains traces of carbon bisulphide and nitrogen pentasulphide. It dissolves without alteration in concentrated sulphuric acid, and has properties similar to those of pseudocyanogen sulphide, $C_3N_3S_3H$. The formation of the pentasulphide takes place according to the equation $N_4S_4 + 2CS_2 = N_2S_5 + S + 2CNS$. The pentasulphide is also formed by heating a mixture of nitrogen sulphide and carbon tetrachloride, an amorphous black bye-product being also formed containing carbon, nitrogen, sulphur and chlorine; this quickly decomposes on exposure to the air with evolution of sulphurous anhydride. It is also produced by reducing with zinc dust thiotrithiazyl chloride, N_3S_4Cl, suspended in methylic alcohol; and generally by the decomposition of nitrogen sulphide and its derivatives; for instance, when nitrogen sulphide is exploded by friction, when the compounds of nitrogen sulphide with the halogens, or with nitrous or nitric acid are boiled with water, and when nitrogen sulphide is heated cautiously with lead oxide. It is not, however, formed by heating nitrogen sulphide with ether or benzene at 110°—125° in a sealed tube; in this case, the greater part of the sulphide is decomposed into nitrogen and sulphur. With ether, a small quantity of a compound having an odour resembling that of acetamide is formed, and with benzene a small quantity of a compound having the characteristic odour of "oleum absynthii."

Nitrogen pentasulphide is a deep red liquid, does not wet glass, has a sp. gr. = 1·901 at 18°, is partially decomposed when distilled even under diminished pressure, solidifies in a freezing mixture to a crystalline mass resembling iodine, and melts at 10—11°. It is insoluble in water, but soluble in most organic solvents, and is stable in solution provided it is not exposed to light; in the latter case, it decomposes into nitrogen sulphide and sulphur. The pure compound quickly decomposes into nitrogen sulphide and sulphur. The absorption spectrum of the solution shows a broad band extending from the D-line into the blue. When boiled with water, a small quantity distils unchanged, but the remainder is converted into ammonia and sulphur. Alkalis decompose it completely in a similar way. When a very minute quantity

of alcoholic potash or soda is added to the alcoholic solution, an intense but transient violet-red coloration is produced, and this reaction is so characteristic that the smallest quantity of the pentasulphide can be detected. When it is added to alcoholic potash, a dark-coloured solution is obtained, from which ether precipitates a yellow, crystalline compound; this is probably a sulphonitrate, and decomposes directly it is removed from the solution. With alcoholic alkali sulphides, it yields polysulphides and ammonia, and with hydrogen sulphide ammonium polysulphide and sulphur. It is violently oxidised by concentrated nitric acid with formation of sulphuric acid; and with dilute hydrochloric or sulphuric acid, it yields ammonium salts and sulphur. E. C. R.

Trimetaphosphimic Acid and its Decomposition Products. By HENRY N. STOKES (*Amer. Chem. J.*, 1896, **18**, 629—663).—A metaphosphimic acid is defined as a metaphosphoric acid $(HPO_3)_n$, in which one-third of the oxygen is replaced by an equivalent number of NH groups.

To prepare trimetaphosphimic acid (Abstr., 1895, ii, 217), the *sodium* salt, $P_3N_3O_6H_3Na_3 + 4H_2O$, is first isolated by shaking a solution of 30 grams of triphosphonitrilic chloride $(P_3N_3Cl_6)$ in 150 c.c. of ether with a solution of 110 grams of sodium acetate crystals in 200 c.c. of water; after agitation for 80 hours, the new salt will have crystallised. When formed at temperatures below 80°, the crystals are orthorhombic (measurements given), with $4H_2O$; above 80° they are microscopic flat prisms, with $1H_2O$. The salt is neutral to litmus. When it is dissolved in an excess of caustic soda solution and the liquid is concentrated, the *tetra-sodium* salt, $P_3N_3O_7H_4Na_4 + H_2O$, crystallises in long, brittle needles which are very unstable, being easily decomposed by carbonic anhydride. Salts with fewer than three or more than four sodium atoms could not be prepared.

The *potassium* salt, $P_3N_3O_6H_3K_3$, the *ammonium* salt, $P_3N_3O_6H_3(NH_4)_3 + H_2O$, the *magnesium* salt, the *barium* salt, and the *barium sodium* salt, $P_3N_3O_6H_3NaBa + 1\frac{1}{2}H_2O$ (?), are described.

The *silver* salt, $P_3N_3O_6H_3Ag_3$, is precipitated by adding silver nitrate to a solution of the sodium salt; in the presence of nitric acid, it separates slowly in the form of colourless, monoclinic plates (measurements given); it is soluble in ammonia. When the tetrasodium salt is used, and the silver nitrate is added in excess, the salt $P_3N_3O_6H_2Ag_4$ (or $P_3N_3O_7H_4Ag_4$) is formed as a white precipitate which changes into the yellow, crystalline salt, $P_3N_3O_6Ag_6$ (or $P_3N_3O_7H_2Ag_6$), when left under pure water. A red, crystalline salt of the same formula was also obtained.

Trimetaphosphimic acid is prepared by decomposing the silver salt with hydrogen sulphide; it is a gummy mass, distinguished from metaphosphoric acid in that it does not coagulate albumin. The final products of the hydrolysis of this acid are ammonia and orthophosphoric acid, but the intermediate products, diiminotriphosphoric acid, iminodiphosphoric acid, and pyrophosphoric acid, have been isolated. To separate these, advantage is taken of the insolubility of magnesium iminodiphosphate, pyrophosphate, and orthophosphate, and the solubility

of magnesium diiminotriphosphate in a feebly ammoniacal solution. The filtrate from the magnesium precipitate may be neutralised and treated with silver nitrate, to obtain silver diiminotriphosphate, from which the sodium salt may be isolated by treatment with sodium chloride. The magnesium precipitate is dissolved in dilute nitric acid, ammonia is added to the solution until incipient precipitation occurs, and then an excess of silver nitrate, whereby silver iminodiphosphate is chiefly precipitated; it must be purified by dissolving it in ammonia, reprecipitating as the magnesium salt, and repeating the process.

Trisodium diiminotriphosphate, $P_3N_2O_8H_4Na_3$, is precipitated in the form of microscopic, flat, pointed prisms or rhombic plates on adding alcohol to its aqueous solution; it is neutral. The *silver* salt, $P_3N_2O_8H_4Ag_3$, forms colourless, monoclinic crystals (measurements given), which are easily soluble in ammonia, but only sparingly so in dilute nitric acid. The salt, $P_3N_2O_8H_2Ag_5$, is precipitated in a white, amorphous form when an ammoniacal solution of the sodium salt is added to an excess of silver nitrate solution.

Trisodium iminodiphosphate, obtained by decomposing the silver salt, is precipitated by alcohol from its aqueous solution as a syrup which dries to a gummy mass; it is alkaline. *Silver iminodiphosphate*, $P_2NO_6H_2Ag_3$, is a white precipitate characterised by its granular form; the salt, $P_2NO_6HAg_4$, exists in a white and a yellow form. The *magnesium, ferric* and *cupric* salts are also described.

In discussing the constitution of the foregoing acids, the author expresses the opinion that Gladstone's pyrophosphodiamic acid (this Journal, 1868, 67) is trimetaphosphimic acid, and his pyrophosphamic acid iminodiphosphoric acid. Trimetaphosphimic acid probably has the constitution expressed by the formula $PO(OH){<}\genfrac{}{}{0pt}{}{NH\cdot PO(OH)}{NH\cdot PO(OH)}{>}NH$. Imino-diphosphoric acid and di-iminotriphosphoric acid are regarded as $PO(OH)_2\cdot NH\cdot PO(OH)_2$ and $PO(OH)_2\cdot NH\cdot PO(OH)\cdot NH\cdot PO(OH)_2$ respectively.

A. G. B.

Compounds of Phosphorus with Selenium. By WILHELM MUTHMANN and A. CLEVER (*Zeits. anorg. Chim.*, 1896, **13**, 191—199).—The compounds described are very similar to those of arsenic and selenium (Abstr., 1896, ii, 18). Phosphorus pentaselenide is prepared according to the method described by Bogen (*Annalen*, 1862, **124**, 57), by melting together the theoretical proportions of red phosphorus and selenium in an atmosphere of carbonic anhydride. It is most important that the materials should be thoroughly dried, as otherwise large quantities of hydrogen selenide are formed. Phosphorus triselenide is prepared in a similar way. Both compounds are unstable when exposed to the atmosphere, and absorb moisture with the formation of hydrogen selenide and the corresponding phosphorus acid. The compounds obtained by treating the phosphorus selenides with alkalis are more easily formed and crystallise better than the selenoarsenic salts; the phosphorus selenides also, unlike the arsenic selenides, are capable of forming ammonium compounds with ammonia, ammonium carbonate, and ammonium sulphide, and double salts with magnesia similar to

the compounds obtained from the sulphophosphates. The alkali carbonates decompose the phosphorus selenides whereas they do not decompose arsenic selenide.

Potassium triselenophosphite, $K_2HPSe_3, 2\frac{1}{2}H_2O$, is obtained by the action of potassium hydroxide on phosphorus pentaselenide. It is more easily prepared by gradually adding the powdered triselenide to a cold concentrated solution of potassium hydroxide, cautiously warming the mixture at 75°—78° until solution takes place, and allowing the filtered solution to crystallise in a freezing mixture; if the mixture is heated above 80°, complete decomposition takes place and hydrogen selenide is evolved. It crystallises in highly lustrous octahedra-like forms, which do not, however, belong to the regular system as they show double refraction; it gradually decomposes in damp air with separation of selenium and hydrogen selenide: when heated, it gives off water vapour and hydrogen selenide, whilst selenium, and then selenious acid sublime, leaving a residue of phosphate. It is sparingly soluble in cold water, easily so in hot water, and can be recrystallised from concentrated potassium hydroxide. The aqueous solution is neutral and pale yellow. With dilute acids, it yields hydrogen selenide, and selenium is gradually precipitated. Lead and silver salts give brownish, amorphous precipitates which gradually darken, and the supernatant solution then contains phosphoric acid. Barium salts give a yellow, amorphous precipitate which quickly turns red.

Potassium thioselenophosphite, $2K_2S, P_2Se_3, 5H_2O$, is obtained by the action of potassium sulphide on the triselenide; it forms small, colourless, doubly-refractive crystals having an octahedral habit and an adamantine lustre, and is decomposed at about the same temperature as the preceding salt with evolution of hydrogen sulphide and selenide. The aqueous solution is colourless, and when treated with acids yields hydrogen sulphide and selenide, whilst a reddish-brown compound mixed with sulphur is precipitated. When treated with salts of the heavy metals, it yields dark, amorphous precipitates.

Sodium oxyselenophosphate, $Na_3PSe_3O + 10H_2O$, is obtained by the action of sodium hydroxide on the triselenide in a similar way to the potassium salts just described. It crystallises from concentrated sodium hydroxide in pale green, doubly-refracting prisms. The aqueous solution quickly decomposes; with acids, it yields hydrogen selenide and a brown precipitate containing selenium. When heated in a tube, it yields a sublimate of selenium, and a phosphate.

All the above substances give well crystallised compounds with ammonia magnesia mixture. E. C. R.

Boric Acid and its Salts. By LOUIS KAHLENBERG and OSWALD SCHREINER (*Zeits. physikal. Chem.*, 1896, **20**, 547—568).—The determination of the molecular depressions due to solutions of boric acid and its salts, lead to the conclusion that in aqueous solution only the one boric acid exists, namely H_3BO_3, and this is formed if the anhydride or a partial anhydride is dissolved. A solution of borax is identical with the solution containing equivalent quantities of boric acid and sodium hydroxide. By the determination of the conductivity and of

the E.M.F. of borate chains, the number of ions present in the solutions was determined, and the conclusions arrived at are that in concentrated solutions of borax there are present sodium ions and anions containing 2 atoms of boron. These anions are, by dilution, dissociated so that in dilute solutions sodium ions and anions containing 1 boron ion are present, and also undissociated boric acid. A solution of sodium metaborate is identical with a solution of boric acid with the equivalent quantity of sodium hydroxide, or to borax solution with sodium hydroxide; the solution contains very few hydroxyl ions and is only slightly decomposed by water. By the addition of more sodium hydroxide, only small quantities of higher compounds are formed, since almost the calculated excess of hydroxyl ions are found in the solution.

The nature of the reaction of borates with polyvalent alcohols was also investigated. The addition of 2 molecules of mannitol to 1 molecule of borax in solution has little effect on the freezing point depression, which is increased by further addition of mannitol; it, moreover, causes the solution to become acidic. If the solution contains sodium hydroxide as well as borax, the addition of mannitol at first decreases the depression, and the results are best explained on the assumption of the formation of a complex anion containing 2 boron atoms and 1 molecule of mannitol, which on adding more of the latter yields an anion containing 2 boron atoms and 2 mannitol molecules; no further combination, however, occurs, so that after this stage is reached the depression is increased. The effects of the addition of mannitol, erythritol, glycerol, and glycol on the electrical conductivity of solutions of borax were also determined, and diagrams representing the results are given. These effects further support the freezing point evidence of the formation of complex ions. L. M. J.

Attempt to Liquefy Helium. By KARL OLSZEWSKI (*Ann. Phys. Chem.*, 1896 [2], **59**, 184—192).—Helium from clèveite of density 2·133 from which all gases that are absorbed by magnesium, copper oxide, phosphoric anhydride and caustic soda had been removed, was cooled down by boiling ethylene and afterwards by boiling air first to $-150°$ and then to $-220°$. It was submitted at the lower temperature to a pressure of 140 atmospheres and the pressure then suddenly reduced to 20 atmospheres, but the gas showed no sign of liquefaction. With the help of the well-known equation $T/T_1 = (p/p_1)^{\frac{k-1}{k}}$ the author calculates the boiling point of helium as below $-264°$, or at least 20° lower than that of hydrogen. The monatomic character of the helium molecule probably accounts for the fact that this gas although of greater density than hydrogen has the lower boiling point.

A comparison of the helium and hydrogen thermometers for temperatures between $-182°$ and $-210°$ shows a very fair agreement, and that therefore the coefficient of expansion of hydrogen remains the same even at these low temperatures. H. C.

Combination of Argon with Water. By P. VILLARD (*Compt. rend.*, 1896, **123**, 377—379).—When carefully purified argon is compressed at 150 atmospheres in presence of water cooled to about 0°, and the water is

further cooled so that it solidifies at one point, combination takes place between the gas and the water with production of a crystalline hydrate similar to those formed by many other gases. Mere compression of the gas in presence of water is not sufficient, but the presence of previously formed crystals of the hydrate has the same effect as the freezing of a small quantity of the water.

The tension of dissociation of the hydrate is 105 atmospheres at 0° and 210 atmospheres at 10°. C. H. B.

A form of Silver obtained on the Reduction of the Sulphide by Hydrogen. By FRANCIS C. PHILLIPS (*J. Amer. Chem. Soc.*, 1894, **16**, 700—703).—If silver chloride is heated in hydrogen to 300°, reduction occurs, and the metallic silver appears as a compact, rounded mass having a moderate lustre. Precipitated silver sulphide when heated to temperatures above 450° in hydrogen, is reduced and the dull black powder gradually changes into a mass of tangled wires or threads which exhibit the lustre of highly polished silver. The wires vary in thickness from that of the finest hairs to that of coarse sewing-thread; and they are often so knotted and linked together as to be almost inextricable. Argentite behaves in a similar manner, but stephanite, Ag_5SbS_4, yields no silver even when heated in hydrogen to dull redness. Artificial copper sulphide when slowly reduced at about 600° yields lustrous threads of copper resembling those obtained in the case of silver. Compare Opificus (*Chem. Zeit.*, 1888, 649), Bischof (*Annalen*, 1843, 289), and Hampe (*Chem. Zeit.*, 1893, 1692).

J. J S.

Oxidation of Silver. By CHARLES E. WAIT (*J. Amer. Chem. Soc.*, 1896, **18**, 254—259).—The author has previously drawn attention to the fact that a certain bismuth litharge from a Western smelting company contained a large amount of silver (2·94 per cent.). It was also shown that the silver was not in the metallic state but was probably present as the oxide, since it readily dissolved in warm acetic acid. In order to account for the formation of the silver oxide, the author has studied the action of various metallic oxides on silver at fairly high temperatures. He finds that manganese dioxide readily oxidises metallic silver to the oxide. Experiments have shown that, other conditions being equal, the longer the duration of the heating the less silver oxide is formed. 0·5 gram of silver, and 2 grams of manganese dioxide, when heated for 2·5 mins., gave 34·28 per cent. of the silver in the form of oxide, but when heated for 20 mins. gave only 11·72 per cent.

Oxides of iron, bismuth, copper and zinc cannot bring about this oxidation, but lead monoxide and dioxide and barium peroxide can. The lead monoxide no doubt acts as an oxygen carrier, and the presence of silver oxide in certain litharges is to be attributed to the oxidising influence of the litharge. J. J. S.

Hydraulic Cements. By ORAZIO REBUFFAT (*Gazzetta*, 1896, **26**, ii, 242—244).—The author replies to Oddo's criticisms (Abstr., 1896, ii, 246). W. J. P.

Atomic Weight of Magnesium. By THEODORE W. RICHARDS and H. G. PARKER (*Zeits. anorg. Chem.*, 1896, **13**, 81—100).—The methods employed consist in determining the weight of silver chloride obtained by precipitating a known weight of magnesium chloride with excess of silver nitrate: also by precipitating a known weight of magnesium chloride with the calculated quantity of pure silver dissolved in nitric acid and then by means of two equivalent solutions of silver and ammonium chloride (the silver solution = 1 milligram per c.c.) determining the point at which equal addition of the two equivalent solutions produces an equal turbidity in the clear supernatant liquid. This point is determined by means of a nephelometer and the method is delicate enough to indicate the difference between 0·002 and 0·003 milligram of silver chloride. All the operations of precipitation, &c., are performed in orange-coloured light.

Pure magnesium chloride free from water, oxychloride or ammonium chloride is obtained by heating magnesium ammonium chloride contained in a platinum boat in a current of perfectly dry hydrogen chloride, at first cautiously, so as to remove any water that may be present: the temperature is then raised and the ammonium chloride volatilised, finally the magnesium chloride is heated to redness until it melts to a clear, colourless liquid. It is then cooled in a current of dry nitrogen, and when cold, the nitrogen is displaced by a current of dry air; the pure dry magnesium chloride is transferred to a weighing bottle without removing it from the drying apparatus. A full description, with drawings of the apparatus, is given in the original paper. The greatest care must be taken to exclude every trace of moisture, as otherwise oxychloride is formed.

The following results were obtained. Series I. (5 experiments) the ratio $2AgCl : MgCl_2$ gave Mg = 24·369. Series III. (6 experiments) the ratio $2Ag : MgCl_2$ gave Mg = 24·365. Series IV. (6 experiments) the ratio $2Ag : MgCl_2$ gave Mg = 24·362. The individual results of Series IV. agree extremely well with one another, the greatest difference amounting to only one-tenth of a milligram of magnesium chloride. Hence the authors accept the last value as the probable atomic weight of magnesium; this compared with the atomic weight of oxygen gives O = 16. Mg = 24·362 : O = 15·96, Mg = 24·301 : O = 15·88, Mg = 24·179.

E. C. R.

Magnesium Nitride. By A. SMITS (*Rec. Trav. Chim.*, 1896, **15**, 135—137. Compare Abstr., 1894, ii, 16).—When an intimate mixture of magnesium nitride, Mg_3N_2, and anhydrous nickel chloride is heated gently in a sealed tube, a brisk reaction takes place; the product after washing with warm water forms a black mass which, when dissolved in mineral acids, yields a green solution, containing ammonia; the black compound is therefore, probably, a nitride of nickel. Anhydrous ferrous, ferric, and cobalt chlorides behave in a somewhat similar manner, except that the black compounds formed are free from nitrogen. Chromic chloride yields a nitride, CrN, which is not acted on by acids at the ordinary temperature; this forms small black plates.

Mercuric chloride yields a green nitride of mercury which is decomposed by acids. Silver nitrate gives a yellow silver nitride which is decomposed by water, yielding silver oxide and ammonia. Platinic chloride when heated with magnesium nitride, even at a low temperature, yields metallic platinum. Cupric oxide or sulphate yields a greenish yellow nitride or at higher temperatures metallic copper. Lead peroxide and the oxides of iron also react vigorously with magnesium nitride. J. J. S.

Corrosion Phenomena of Zinc Plates. By FRANZ MYLIUS and ROBERT FUNK (*Zeits. anorg. Chem.*, 1896, **13**, 151—156).—Cast zinc and cadmium anodes which are contaminated with a layer of oil or grease, when subjected to a current of 1 ampère per square decimetre in a bath of zinc sulphate, are pitted and the skin is undermined by the action of the electric current in such a way that a thin skin is separated. Rolled zinc plates suffer a like corrosion, which is probably due to the mixing of the impurities contained in the zinc by the process of rolling. The corrosion of zinc containing lead is hindered by sudden cooling when cast and by the mechanical treatment of rolling. The mechanical treatment of pure zinc has, however, a very slight influence on the ease with which corrosion takes place. An analysis of the outer skin and the inner layer of a commercial zinc plate gave practically the same percentage composition, so that the corrosion phenomena cannot be due to a difference in the composition of the outer skin. E. C. R.

Zinc Carbonate. By KARL KRAUT (*Zeits. anorg. Chem.*, 1896, **13**, 1—15).—The author has determined the composition of the products obtained by precipitating zinc salts with alkali carbonates, and hydrogen carbonates under varying conditions. The first product obtained when solutions of these salts are poured into solutions of zinc sulphate is normal amorphous zinc carbonate. This, according to circumstances, is then either converted into the stable crystalline zinc carbonate, $ZnCO_3,H_2O$, or into the basic carbonate, $5ZnO,2CO_2,4H_2O$, with evolution of carbonic anhydride. The basic zinc carbonate, $2ZnO,CO_2$, described by Boussingault, Wackenroder, and H. Rose, and probably all the basic carbonates having compositions between the compounds ZnO,CO_2 and $5ZnO,2CO_2$, are mixtures formed by the partial conversion of the primary amorphous zinc carbonate into crystalline carbonate and into the basic carbonate, $5ZnO,2CO_2,4H_2O$. If the solution of the zinc salt is added to a solution of alkali carbonate, the normal carbonate is not formed, but only the basic carbonate, and this is due to the presence of an excess of alkali carbonate during the precipitation. Finally, the basic carbonate, when boiled with excess of alkali carbonate, is converted into anhydrous zinc oxide.

Basic zinc carbonate, $5ZnO,2CO_2,4H_2O$, can be obtained pure by dissolving zinc, hydrated zinc oxide, or zinc carbonate in an excess of aqueous carbonic acid and then boiling the solution, when it is precipitated. It is also obtained very nearly pure by precipitating zinc sulphate with an alkali carbonate from cold dilute solutions or from boiling solutions, if equivalent quantities of both salts are em-

ployed. Concentration of the solutions determines the formation of the normal carbonate, and dilution, the formation of the basic carbonate; above a certain concentration, excess of potassium or sodium hydrogen carbonate combines with the zinc carbonate to form double salts.

A solution of zinc sulphate in water was mixed with a solution of sodium hydrogen carbonate in water, in the proportion $ZnSO_4$: $4NaHCO_3$; the precipitate was allowed to remain under the mother liquor until it had become crystalline, then collected, and washed with a solution of sodium hydrogen carbonate. It consisted of small quadratic optically active crystals of zinc carbonate, $ZnCO_3,H_2O$, and of larger octahedral skeleton forms which were inactive, and gave on analysis numbers agreeing with the formula $Na_2O,3ZnO,4CO_2,3H_2O$. The two compounds can easily be separated mechanically.

The author was unable to prepare a basic carbonate of cadmium. Only a very small quantity of cadmium carbonate is dissolved by aqueous carbonic acid, even under a pressure of several atmospheres. The precipitate obtained by adding cadmium sulphate to a solution of sodium carbonate consists of cadmium carbonate, $CdCO_3$, mixed with a small quantity of the basic sulphate, $2CdO,SO_3$; whilst by adding cadmium nitrate to an excess of ammonium carbonate, the carbonate $CdCO_3 + \frac{1}{2}H_2O$ is obtained. E. C. R.

Electrolytic Refining of Cadmium. By Franz Mylius and Robert Funk (*Zeits. anorg. Chem.*, 1896, **13**, 157—160).—The electrolytic refining of cadmium is carried out in a very similar way to that of zinc. The cadmium is deposited from a concentrated solution of cadmium sulphate, slightly acidified, on cathodes of platinum or cadmium foil, a current density of 0·5—1 ampère per square decimetre being employed. The deposited cadmium is easily separated from the cathodes, and when melted and sublimed in a vacuum is obtained in flat needles or silvery six-sided tablets. No impurities can be detected by chemical means in the metal so prepared.

The lead in the impure metal is completely separated by electrolysis of the sulphate solution with a very weak current, and is deposited partly at the cathode as metal and partly at the anode as peroxide. Iron is most easily detected by means of potassium thiocyanate. The presence of zinc is detected by melting a sample of the metal in a porcelain crucible and breaking the skin of oxide with a glass rod, so that the bright molten metal is exposed; if the cadmium is free from zinc, the bright surface in a few seconds becomes covered with a many-coloured oxidation skin; in the presence of zinc, however, the oxidation of the cadmium is hindered, and zinc oxide is first formed. This reaction is so delicate that less than 0·01 per cent. of zinc can be detected.

The quantitative estimation of the zinc in cadmium is effected by transferring the cadmium electrolytically through a very dilute acid or salt solution, whereby the whole of the zinc remains in solution together with a small quantity of cadmium, and can now be easily separated from the latter. E. C. R.

Crystallised Slags from Copper-smelting. By Alfred C.

LANE (*Bull. Geol. Soc. Amer.*, 1895, **6**, 469—470).—At the smelting works at Dollar Bay and on Torch Lake in Upper Michigan, the copper which has been oxidised during the melting down of the ore is afterwards reduced. The slag produced in this reduction has a strong tendency to crystallise, and contains very large melilite crystals in the form of square tablets with rounded and reticulated faces. The crystals are optically uniaxial and negative; they are merely shells, with a rectangular network of enclosed matter, consisting of a greenish birefringent substance, iron oxides, and globules of copper; a partial analysis, by R. L. Packard, gave

SiO_2.	Fe_2O_3.	Al_2O_3.	CaO,MgO, &c. [diff.].
34·84	16·78	13·26	[35·12]

In cavities in the slag are small scales of hæmatite. L. J. S.

Solubility of Lead and Bismuth in Zinc. By WALTHÈRE SPRING and L. ROMANOFF (*Zeits. anorg. Chem.*, 1896, **13**, 29—36).—A crucible is prepared with a hole bored in the side at a convenient distance from the bottom and stopped with a plug during the preparation of the solution. The crucible is filled with the heavier metal (lead or bismuth) so that the level of the molten metal is just above the hole, the zinc is then added, covered with a protecting layer of fused salt or charcoal, and the crucible maintained at the temperature at which the solubility is to be determined. The contents are stirred about every 10 minutes. The sample of the top layer is taken by bailing out a sufficient portion. The plug is then knocked out of the side of the crucible, and after the top layer has run out, a sample of the bottom layer is bailed out. A table of the composition of the two layers at temperatures from 266—900° is given. When the results are stated graphically, taking the temperature for abscissæ and the percentage of the two layers as ordinates, two points are obtained for each temperature: one the solubility of bismuth in zinc, the other the solubility of zinc in bismuth, and by prolonging these two until they meet, the temperature is determined at which the two metals will mix in all proportions. The critical temperature for bismuth and zinc lies between 800—850°, that for lead and zinc between 900—950°. The curves are analogous to those obtained by Alexéeff for non-miscible liquids. E. C. R.

Metaplumbates. By M. HOEHNEL (*Arch. Pharm.*, 1896, **234**, 397—400).—Calcium metaplumbate (Abstr., 1896, ii, 248) is much more stable than the metaplumbates of sodium and potassium; by digesting it with a solution of the acetate of a heavy metal, the metaplumbate of that metal can be prepared. The following were obtained in this way: *metaplumbate* of *zinc*, $ZnPbO_3 + 2H_2O$, reddish-brown, crystalline; of *copper*, $CuPbO_3$, black, amorphous; of *manganese*, grey-black, crystalline; of *lead*, $PbPbO_3$, reddish-brown, amorphous, and identical with lead sesquioxide. C. F. B.

Potable Waters which have flowed through Lead Pipes. By UBALDO ANTONY AND T. BENELLI (*Gazzetta*, 1896, **26**, ii, 97—107, 352—362).—The authors have examined the action of water of various

degrees of purity on lead, and have obtained analytical results which are summarised in the accompanying table.

	Parts of lead per 100,000.			
	1	2	3	4
Water alone, unfiltered	8·19	12·98	8·19	4·09
Water alone, filtered	3·00	4·09	2·07	2·32
Water containing chlorides, unfiltered	1·36	2·73	0·68	4·09
Water containing chlorides, filtered	0·68	1·50	0·67	1·36
Water containing sulphates, unfiltered	3·41	6·83	2·05	1·84
Water containing sulphates, filtered	2·05	3·41	1·64	1·77

Water was allowed to remain in contact with lead wire for five days, each 150 c.c. of water being in contact with 285 square cm. of metal. The amount of lead in the unfiltered and filtered water was then determined. The column headed 1 gives the numbers for distilled water free from air,—first for the pure water, then for water containing 0·049 gram of sodium chloride per litre, and finally for water containing 0·49 gram of sodium sulphate per litre; column 2 gives the corresponding data for distilled water aërated by agitation with air; column 3 shows the results obtained with water continuously aërated by passing 1 litre of air through it per hour, whilst column 4 gives the data for distilled water through which 1 litre of air and 400 c.c. of carbonic anhydride were passed per hour throughout the experiment. The lead was determined by the process previously described by the authors (Abstr., 1895, ii, 549).

The authors next experimented on the solubility of lead in water containing various dissolved substances, with the results summarised in the accompanying table.

Water used.	Parts of lead per 100,000.			
	1	2	3	4
Distilled water alone	8·19	12·98	8·19	4·09
Distilled water with NaCl	1·36	2·75	0·68	4·09
Distilled water with Na_2SO_4	3·41	6·83	2·05	1·84
$CaHCO_3$ solution alone	2·45	3·14	2·63	5·70
$CaHCO_3$ solution with NaCl	2·05	3·41	2·35	3·40
$CaHCO_3$ solution with Na_2SO_4	2·18	3·32	2·05	3·16
$CaSO_4$ solution alone	6·83	6·83	3·41	1·35
$CaSO_4$ solution with NaCl	5·46	6·57	3·51	1·50
$CaSO_4$ solution with Na_2SO_4	4·78	5·87	3·69	1·77

The experiments were conducted under conditions similar to those prevailing in the earlier experiments. Columns 1, 2, 3, and 4 refer to the solutions named in the first column (1) free from air; (2) saturated

with air; (3) continuously aërated by a current of air; and (4) continuously aërated by a current of air and carbonic anhydride; the quantities of sodium chloride and sulphate present in the various samples of water were the same as before. In the experiments with solutions of calcium hydrogen carbonate, each litre contained 0·04 gram of CaO as carbonate, whilst in the tests with calcium sulphate, each litre of water contained 0·095 gram of CaO as sulphate. W. J. P.

Double Chlorides. By RAOUL VARET (*Compt. rend.*, 1896, **123**, 421—423).—The double chlorides formed by mercuric chloride $2HgCl_2,MCl_2 + nH_2O$, and $HgCl_2,MCl_2 + nH_2O$ are all more or less dissociated when their solutions are submitted to dialysis. The author finds that when dilute solutions of mercuric chloride and various metallic chlorides are mixed, there is a development of heat which varies in different cases from 0·80 to 1·36 Cal., but generally approximates somewhat closely to 1·0 Cal. The double salts may be regarded as derived from two complex unstable acids, H_2HgCl_4 and $H_2Hg_2Cl_6$.

Solutions of cupric or cadmium chloride give practically no thermal disturbance when mixed with solutions of other metallic chlorides, and when solutions of the double chlorides of copper or cadmium are dialysed, the proximate constituents can be completely separated. It follows that these double salts exist as such in the solid state only.

C. H. B.

The Components of Monazite. By G. PAUL DROSSBACH (*Ber.*, 1896, **29**, 2452—2455).—The monazite examined came from the Blue Mountains. It was finely powdered, and then decomposed with sulphuric acid; from the solution, the thorium was separated by fractionation, and then a large excess of sulphuric acid was added. The erbium metals remain in solution, whilst the cerium metals are precipitated; their precipitation is rendered more complete by partially neutralising the liquid with soda, for with sodium sulphate, they form double salts which are quite insoluble in a saturated solution of that salt.

The solution of the cerium metals is then treated with potassium hydroxide and permanganate, which precipitates the cerium as the dioxide, together with some of the didymium; the latter is extracted, with dilute nitric acid: strong nitric acid then extracts the cerium, leaving the manganese dioxide. The lanthanum and didymium in solution are converted into nitrates, and these are fractionally precipitated with sodium hydroxide; didymium is first precipitated, as the basic nitrate, whilst the lanthanum remains in solution. Perhaps the two didymium precipitates obtained contain different elements.

The erbium elements in solution are precipitated with oxalic acid; the oxalates are converted into the hydroxides, and these into the nitrates, which are then fractionally precipitated with magnesia. Yttrium remains in solution; from the precipitate, ytterbium can first be separated by the basic nitrate method, and erbium next fractionally precipitated with dilute sodium hydroxide, when the solution is found

to contain what is possibly a new element, with an atomic weight in the neighbourhood of 100. C. F. B.

Analyses of Steel.—By GIOVANNI GIORGIS and UGO ALVISI. (*Gazzetta*, 1896, **26**, ii, 167—178).—The authors have analysed a number of specimens of soft steel, the mechanical properties of which have been studied by Biadego (*Rivista Tecnica L'Industria*, 1895, **47**, **52**; 1896, **2**, **6**, **7**). W. J. P.

Steel.—By FRANZ MYLIUS, FRITZ FOERSTER and GEORG SCHOENE (*Zeits. anorg. Chem.*, 1896, **13**, 38—58).—*Iron Carbide in Steel.*—The iron carbide was at first extracted from tool-steel by electrolysis. Anodes of steel plates or rods are subjected to a current of 1 ampère per quarter-decimetre in a bath of concentrated zinc sulphate containing 0·1 per cent. of free acid. The electrolysis proceeds without any appreciable evolution of hydrogen, but the anode becomes coated with a grey skin which must be occasionally rubbed off. The residue obtained consists of a grey powder which contains from 7 to 9 per cent. of carbon and about 90 per cent. of iron. It is not, however, pure carbide; for whilst the steel dissolves completely in hot hydrochloric acid, this residue contains a small quantity of insoluble carbonaceous material. The carbide was also extracted with twice normal, and with normal sulphuric acid at the ordinary temperature, washed as quickly as possible with water, alcohol, and finally with ether, and dried at 120° in a current of hydrogen, care being taken to exclude air as much as possible during the operations. Four experiments with the same steel gave products which contained from 6·5 to 7·2 per cent. of carbon, and were not completely soluble in hot hydrochloric acid, but yielded a small carbonaceous residue; this residue is formed by the oxidation of the damp carbide on exposure to air. In order to obtain an iron carbide completely soluble in hydrochloric acid, the steel is extracted on a filter bed of asbestos with sulphuric acid in an apparatus so arranged that the extraction is performed in an atmosphere of hydrogen. The residue is washed in the same apparatus with water, alcohol, and ether in an atmosphere of carbonic anhydride, and dried at 100° in a current of carbonic anhydride. This product is almost completely soluble in hydrochloric acid; the residue, which amounts to 0·1 per cent., consists of silica. It gave on analysis—6·5 per cent. C, 91·96 per cent. Fe, 1·1 per cent. Mn, 0·23 per cent. Cu, 0·02 per cent. Si, and traces of sulphur, phosphorus, arsenic and nickel. When heated to redness in a current of nitrogen or hydrogen, it lost only 0·4 per cent. in weight.

Iron carbide, when dry, is not altered by exposure to air. When dried at 100° in a current of hydrogen, and then exposed to air, it glows and yields iron oxide; the same phenomenon occurs occasionally when it is dried at a low temperature in carbonic anhydride or nitrogen. When heated to redness in hydrogen, it is not pyrophoric; but the hydrogen must be completely displaced by carbonic anhydride or nitrogen to render it stable on exposure to air. When damp, it is rapidly oxidised on exposure to air, yielding a brown powder, which consists of a mixture of oxide of iron and the carbon compound $C_{12}H_6O_3$ described by

Bourgeois and Schützenberger (this Journal, 1875, 788) and by Zabudzky (Abstr., 1882, 427, 660). This compound is most easily obtained by treating the carbide with a solution of ammonium sulphate in dilute sulphuric acid. The carbide is only slightly decomposed when heated with water at 145°, but when heated at 400° to 430° in a current of steam and nitrogen for half an hour, it increases 13 per cent. in weight and yields a black residue containing oxides of iron and free carbon together with a combustible gas consisting for the most part of hydrogen. When heated at a red heat in a current of steam for half an hour, it increases 29 per cent. in weight, yields a black powder of ferrosoferric oxide and a gaseous mixture of hydrogen, carbonic oxide and carbonic anhydride. It is not appreciably attacked by very dilute acids; when treated with one-tenth normal hydrochloric acid at 80°, a distinct evolution of hydrogen is observed. It is very gradually dissolved by normal hydrochloric acid, and 1 gram after remaining sealed up in a vacuum tube for 10 days with normal hydrochloric acid gave only 2·5 c.c. of a combustible gas. In concentrated hydrochloric acid, it is easily soluble and leaves only a minute residue which is insoluble in water, but easily soluble in alcohol or ether. In no case did the authors observe the formation of amorphous intermediate carbonaceous products during the dissolution. An analysis of the gas evolved on dissolving the carbide in hydrochloric acid gave 92·3 per cent. H, 6·3 per cent. hydrocarbons, 1·4 per cent. N. The ratio of the combined hydrogen to the carbon very nearly approaches that required for a member of the series C_nH_{2n+2} and the density of the hydrocarbon is about the same as that of pentane. Although the iron carbide is not altered by heating to redness, it melts at a white heat in an atmosphere of nitrogen, and carbon is deposited. The cast iron regulus thus obtained contains 4·36 per cent. of carbon; it is very brittle, shows a radial fracture like that of "spiegeleisen," and contains no graphite.

In order to prove that the iron carbide is present in the steel as a definite chemical compound, the authors extracted samples of the steel with various acids of different strengths. Normal acetic acid yielded the best results, over 90 per cent. of the carbon present in the steel being obtained as carbide; whilst with N × 4 hydrochloric acid only 25 per cent. of the carbide was obtained. The product, in all cases, contained the same percentage of carbon. Samples prepared from different sorts of steel gave the same composition on analysis as did also a sample prepared from carbonised iron, made in the laboratory from pure electrolytic iron which was carbonised by means of pure acetylene.

It is evident from the above results that the carbide is a definite chemical compound of the formula Fe_3C. Only in one reaction does it show a behaviour different from that which one would expect from a compound of the formula Fe_3C, which should decompose when treated with acids according to the equation $Fe_3C + 6HCl = 3FeCl_2 + CH_4 + H_2$.

E. C. R.

Crystallised Martin-slag. By A. Harpf (*Jahrb. f. Min.*, 1896, ii, Ref. 37; from *Österr. Zeits. f. Berg- und Hüttenwesen*, 1895, No. 7).—

Crystallised slag from the Martin-furnace at the iron and steel works at Donawitz, gave the following results on analysis :—

SiO_2.	FeO.	Al_2O_3.	MnO.	CaO.	MgO.	Fe.	Total.	sp. gr.
30·75	60·23	2·07	5·10	1·30	1·10	0·07	100·62	4·280.

This shows the material to be fayalite. Some of the crystals are tabular, others are columnar ; they show the forms *b* {010}, *c* {001}, *d* {110}, *s* {102}, and *z* {104}. L. J. S.

New Cobalt and Nickel Salts. By NAGENDRA CH NÂG (*Zeits. anorg. Chem.*, 1896, **13**, 16—18. Compare Durrant, Proc., 1896, 96 and 244).—When precipitated, cobalt carbonate is treated with bromine in presence of potassium hydrogen carbonate, carbonic anhydride is evolved, and a green solution is formed, from which a green compound, which does not contain bromine, is precipitated by shaking the solution with alcohol and ether. The new compound is very unstable and has not yet been isolated, but it appears to be an oxidation product probably corresponding to the ferates. A nickel compound was not obtained under like conditions.

When either cobalt or nickel carbonate is treated with sodium acetate and bromine, a deep orange-red solution is obtained. The nickel solution when boiled gives a violet precipitate and a neutral apple-green solution. The cobalt solution gives no precipitate when boiled. These orange-red compounds appear to be lower oxidation products, for when potassium hydrogen carbonate is added to the brown cobalt salt solution containing an excess of bromine, the green solution is obtained. E. C. R.

Constitution of Cobalt, Chromium and Rhodium Bases. By SOFUS M. JÖRGENSEN (*Zeits. anorg. Chem.*, 1896, **13**, 172—190 ; see also Abstr., 1895, ii, 47 ; 1896, ii, 424).—The author has determined the relative quantities of the compounds formed in the preparation of Erdmann's cobalt triamine nitrite (*J. pr. Chem.*, 1866, **97**, 412), and gives a table of the results. Cobalt carbonate (10 grams) dissolved in hydrochloric acid (50 c.c.), was treated with varying quantities of sodium nitrite and 20 per cent. ammonia and the mixture oxidised in various ways ; the dark brown liquor obtained, was filtered from the insoluble matter and evaporated to dryness in a draught. The residue was dissolved in 50—70 c.c. of cold water, whereby a second residue was obtained, and a dark brown solution which, when treated with dilute nitric acid, yielded the xantho-nitrate. The insoluble residues were washed with cold water until free from chlorine, whereby the croceo- and xantho-chlorides were removed, and the residue free from chlorine was extracted with hot water containing some acetic acid, when the triamine nitrite was dissolved. This was separated from the croceo-diamine nitrite and other sparingly soluble impurities by fractional crystallisation from very dilute acetic acid ; the bulk of the croceo-diamine nitrite was obtained in the last extraction of the residues. The last two salts are more soluble the more concentrated the acetic acid used. Of the salts of the composition $Co(NH_3)_3(NO_2)_3$, only the ordinary triamine nitrite and the croceo-diamine nitrite were obtained.

The best yield of these salts, amounting to one-fourth of the cobalt used, is obtained by employing 27 grams of sodium nitrite and 200 c.c. of 20 per cent. ammonia and passing air through the mixture for two hours and then allowing the mixture to remain for 3 days in an open dish. The relative quantities of the materials employed, the dilution, and especially the method in which the oxidation is effected, have a great influence on the composition of the products obtained.

Different forms of the triamine nitrite and the dinitrotriamine chloride.—The triamine nitrite crystallises, according to the conditions, in needles or in rhombic tablets. The dinitrotriamine chloride crystallises in quadratic tablets, in octahedra, in elongated prisms and in other forms; all these modifications when precipitated with hydrochloric acid are converted into quadratic tablets. The dinitrotriamine chloride is dissociated when dissolved in water, but only to a small degree at the ordinary temperature: when heated with water containing a few drops of acetic acid on the water bath, it yields the triamine nitrite according to the equation

$$2(NO_2)_2Co(NH_3)_3Cl = (NO_2)_2Co(NH_3)_3NO_2 + Co(NH_3)_3(NO_2)Cl_2.$$

The author was unable to obtain an isomeric triamine nitrite by adding sodium nitrite to the solution, and the only compound isolated was ammonium cobalt dinitrite.

Action of dilute acids on croceocobalt-diaminecobalt nitrite.—Croceocobalt-diaminecobalt nitrite is converted by prolonged treatment with hydrochloric acid at the ordinary temperature into a dark brown crystalline powder which consists of the chloronitro-tetramine chloride and *chloronitrotetraminecobalt-diaminecobalt nitrochloride*,

$$NO_2CoCl(NH_3)_4Cl_2(NH_3)_2Co(NO_2)_2.$$

The latter salt is separated by washing the precipitate with water, in which it is insoluble: it is then washed with alcohol (95 per cent.), dried over sulphuric acid, and purified by dissolving it in water and precipitating with hydrochloric acid. When heated with sodium nitrite, it is quantitatively reconverted into the croceodiamine nitrite. The above constitution is proved by the following reactions. When heated with hydrochloric acid, it yields the chloronitrotetramine chloride, and with dilute nitric acid, the aquoxantho-nitrate. When treated with water containing acetic acid, it yields aquoxantho-salts. Silver nitrate precipitates all the chlorine as silver chloride. When heated with water, ammonium nitrate and ammonia, it yields xanthonitrate and flavonitrate. It is also obtained by mixing a solution of the chloronitrotetramine chloride in water containing a small quantity of acetic acid with a solution of the ammonium-diamine nitrite in water and hydrochloric acid. E. C. R.

Action of Chromic Acid on Thiosulphuric Acid. By ANTONIO LONGI (*Gazzetta*, 1896, **26**, ii, 119—141).—In view of the fact that Longi and Bonavia (Abstr., 1896, ii, 625) have shown Diehl's interpretation of the reaction between a chromate and a thiosulphate to be erroneous, the author has examined the reaction in detail. On adding a mineral acid and potassium dichromate to a dilute sodium thiosulphate

solution, the reaction which takes place is in accordance with the equation $2H_2CrO_4 + 6H_2S_2O_3 = 3H_2S_4O_6 + Cr_2(OH)_6 + 2H_2O$, small quantities of sulphuric acid being simultaneously formed in accordance with a secondary reaction expressed by the following equation, $3H_2S_4O_6 + 14H_2CrO_4 + 16H_2O = 12H_2SO_4 + 7Cr_2(OH)_6$. Hydrogen sulphide is also produced, and it is shown that both sodium thiosulphate and tetrathionic acid give this gas when small quantities of an acid or a chromic salt are added to their solutions; more hydrogen sulphide is obtained at high than at low temperatures, and tetrathionic acid is more stable than the thiosulphate, for sodium thiosulphate gives hydrogen sulphide when treated with hydrogen peroxide or acetic acid, or when carbonic anhydride is passed through its hot solution.

W. J. P.

Formation of Antimony Cinnabar. By JOHN H. LONG (*J. Amer. Chem. Soc.*, 1896, **18**, 342—347. Compare Abstr., 1895, ii, 399).—It has been previously shown that antimony cinnabar, obtained by boiling a solution of antimony chloride or tartrate with sodium or calcium thiosulphate, has the composition Sb_2S_3.

On boiling solutions of antimony salts with hydrogen sulphide or an alkali sulphide and sulphurous anhydride, the amorphous sulphide mixed with free sulphur is always formed. A thiosulphate precipitates the cinnabar red product from either acid or neutral solutions of antimony salts, the addition of a few drops of ammonia, however, prevents the precipitation. Antimonious oxide remains unaltered when boiled with a thiosulphate, but on adding a small quantity of hydrochloric acid, the red sulphide is slowly formed; only a small portion, however, of the oxide can be converted into sulphide by this method, notwithstanding the amount of acid added.

Antimony oxychloride readily gives the cinnabar-red precipitate on boiling with a thiosulphate solution, even without the addition of acid.

J. J. S.

Action of Alkali Sulphides on Auric Sulphide. By UBALDO ANTONY and ADOLFO LUCCHESI (*Gazzetta*, 1896, **26**, ii, 350—353).—Auric sulphide, Au_2S_3, dissolves in sodium monosulphide solution at 3—4° giving an odourless, reddish liquid which, however, rapidly becomes yellow and acquires the characteristic odour of the polysulphides. On pouring the odourless solution into absolute alcohol, an oily heavy mass is deposited which rapidly changes into a mass of white needles; the latter consist of *sodium sulphaurite* Na_3AuS_2, which is a comparatively stable substance and apparently results from the reduction of the oily sulphaurate, Na_3AuS_3. Sodium sulphaurite is soluble in water, and the solution gives precipitates with solutions of metallic salts; *silver sulphaurite*, Ag_3AuS_2 is obtained as a heavy reddish precipitate.

Similar results are obtained with potassium monosulphide.

W. J. P.

Purple of Cassius. By UBALDO ANTONY and ADOLFO LUCCHESI (*Gazzetta*, 1896, **26**, ii, 195—196).—On adding a smaller quantity of mercurous chloride to a solution of auric chloride than is required by

the equation $3HgCl + AuCl_3 = 3HgCl_2 + Au$, metallic gold is deposited; but if excess of mercurous chloride be added, that which remains unchanged assumes the characteristic colour of purple of Cassius; similar results are obtained with cuprous chloride. Further, if barium sulphate and mercurous chloride are suspended in water and excess of auric chloride then added, the barium sulphate takes up the gold and becomes the colour of purple of Cassius.

Since these several salts can assume the colour of purple of Cassius, it follows that the true purple of Cassius is not a compound but merely stannic acid mechanically coloured with metallic gold.

W. J. P.

New Double Salt of Platosemidiamine. By DAGMAR SCHOU (*Zeits. anorg. Chem.*, 1896, **13**, 36—37).—A *platosemidiamine chloride carbonate* $2Pt(NH_3)_2Cl_2, Pt_2(NH_3)_4Cl_2CO_3$, is obtained by mixing a solution of potassium platinochloride in water at 40° with a mixture of ammonium hydrogen carbonate and water, and then passing carbonic anhydride through the solution until it acquires an indigo blue colour and some quantity of a blackish-blue precipitate is deposited. The solution is precipitated with alcohol, and the precipitate washed successively with water and alcohol, and dried by exposure to the air. It forms small crystals and aggregates, is sparingly soluble in water, insoluble in alcohol and ether, is gradually decomposed by cold hydrochloric acid, and, by boiling with the acid, is converted into platosemidiamine chloride. When boiled with ammonia, a small quantity remains undissolved, and the solution when saturated with hydrogen chloride and treated with potassium platinochloride gives a precipitate of Magnus's green salt. When treated with a slight excess of silver nitrate, a yellow solution of platosemidiamine nitrate is obtained.

E. C. R.

Iridio-ammonium Compounds. VI. By WILHELM PALMAER (*Zeits. anorg. Chem.*, 1896, **13**, 211—228; see also Abstr., 1889, 352; 1891, 402 and 1165; and 1896, ii, 179).—*Iridiotetramine dichlorochloride*, $Ir(NH_3)_4Cl_3, H_2O$, has been obtained in very small quantities by the action of ammonia on iridium chloride (Abstr., 1896, ii, 179). It is extracted from the mixture thus obtained, together with ammonium chloride, by means of cold water, and is separated from the ammonium chloride by fractional crystallisation from water, or by crystallisation from 40 per cent. alcohol. It crystallises in aggregates of thin, yellowish-white needles, or, when slowly crystallised, in bright yellow prisms belonging to the monoclinic system $a:b:c = 0{\cdot}72078:1:0{\cdot}65354$; $\beta = 53°\ 13'$. The water of crystallisation is not entirely removed by heating at 100°. It is soluble in 15 parts of water at the ordinary temperature, and has the electric conductivity $\mu = 104{\cdot}5$ at 25° ($V = 1000$). When heated, it yields ammonia and ammonium chloride and a residue of metal remains. With concentrated sulphuric acid, one-third of the chlorine is evolved as hydrogen chloride. The *dichlorosulphate*, $[Ir(NH_3)_4Cl_2]_2SO_4,2H_2O$, obtained by treating the preceding compound with concentrated sulphuric acid, crystallises in thin, lustrous, bright yellow scales, gives off ammonia when heated,

and is sparingly soluble in water; the solution has a neutral reaction. The *dichlorochloroiridite*, $3Ir(NH_3)_4Cl_3 + 3IrCl_3$, is a leather-coloured precipitate, insoluble in cold water, and is attacked by concentrated sulphuric acid at 100°.

The insoluble double salt of the empirical formula $Ir(NH_3)_3Cl_3$, obtained by the action of ammonia on iridium chloride (*loc. cit.*), is partly grey and partly leather-coloured. The grey compound is attacked by concentrated sulphuric acid at 100°, the leather-coloured compound partly at 110° and partly at 100°; hence the grey compound is the double salt of aquopentamine chloride, and the leather-coloured compound the double salt of pentamine or tetramine chloride and iridium trichloride.

The reactions of the tetramine salts are described in detail. The *bromide* is precipitated in bright yellow, rhombic crystals, the *aurochloride* in orange-red, four-sided tablets, the platinochloride in bright yellow aggregates. The solutions of the tetramine salts give a violet colouration with chlorine water.

Finally, the author gives a complete *resumê* of the chemical and physical properties of the pentamine, aquopentamine, hexamine, and tetramine compounds of iridium, and compares them with the corresponding compounds of chromium, cobalt, and rhodium. E. C. R.

Mineralogical Chemistry.

Behaviour of Minerals when submitted to the X-Rays. By CORNELIUS DOELTER (*Jahrb. f. Min.*, 1896, ii, 87—106).—The several minerals examined show great differences of transparency for the Röntgen rays, and no general relation between the density and transparency can be traced, but minerals with a density greater than 5 seem to be opaque. Also, no relation can be traced to the chemical composition or molecular weight, but sulphur and arsenic compounds are the most opaque, boron and aluminium compounds, as a rule, the most transparent, and in silicates the opacity increases with the amount of iron. Dimorphous minerals do not show any important differences. Crystals show only slight differences in various directions. A scale of eight degrees of transparency is given:—1 diamond, 2 corundum, 3 talc, 4 quartz, 5 rock-salt, 6 calcite, 7 cerussite, 8 realgar. Boric anhydride is even more transparent than diamond; realgar is quite opaque. For distinguishing between precious stones and their imitations, the method has a practical application. L. J. S.

Heavy Liquids for the Separation of Minerals. By JAN W. RETGERS (*Jahrb. f. Min.*, 1896, i, 212—221).—Penfield (Abstr., 1896, ii, 216) has mentioned that as Retgers' thallium-silver nitrate acts on mineral sulphides, it cannot be used for their separation; this is due to the oxidising action of the nitrate. Blende is energetically attacked by molten silver nitrate with evolution of nitrous fumes, and separation

of metallic silver and zinc sulphate. Thallium nitrate acts on pyrites, but, at a moderate temperature, not on blende. The acetates of thallium, silver, lead, and mercury, and various double and basic salts, as well as mixed acetates and nitrates of these heavy metals, have been examined, but the results are not very favourable, because, although the melting points are usually low, the specific gravity of the liquid is too low for use with mineral sulphides, being rarely above 3—4. Thallium-silver acetate (m. p. 75°, sp. gr. 4·8) becomes opaque owing to separation of metallic silver. Thallium-lead acetate (sp. gr. 3·6) is liquid at the ordinary temperature, and has a high index of refraction. The only ones that would be of any use are thallium acetate (m.p. 110°, sp. gr. 3·9) and thallium nitrate-acetate (m.p. 65°, sp. gr. 4·5); the former, however, owing to its low sp. gr., would be only applicable in a few cases, and the latter decomposes at temperatures above 100°. L. J. S.

Diamondiferous Sand from Brazil. By HENRI MOISSAN (*Compt. rend.*, 1896, **123**, 277—278).—Sand from Brazil, after removal of the siliceous constituents, was found to contain microscopic, transparent diamonds, black diamonds and graphite, together with particles of gold and platinum. It is noteworthy that in Brazil as well as at the Cape the diamonds are associated with graphite. C. H. B.

Free Gold in Granite. By GEORGE P. MERRILL (*Amer. J. Sci.*, 1896, [4], 1, 309—311).—A specimen labelled "gold ore, Sonora, Mexico" is an ordinary black-mica granite which, owing to weathering, is brown and friable; throughout the mass are numerous specks, rarely over 1 mm. in diam., of native gold. Pyrites and other sulphides are not present. Microscopical examination of thin sections of the rock shows the gold enclosed in the quartz and felspar as beautiful arborescent and platy forms; it therefore does not seem to be a secondary constituent which has been deposited along fissures, but to be a primary constituent which has crystallised from the original magma. Such a mode of occurrence of gold does not seem to have been before described. L. J. S.

Nitrogen and Argon in Firedamp and in the Gas from the Rochebelle Coal Seam. By TH. SCHLOESING, Junr. (*Compt. rend.*, 1896, **123**, 302—305).—The firedamp, collected without admixture of air and containing no oxygen, was found to contain the following proportions of nitrogen and argon.

Mine.	Pressure of issuing firedamp in cm. of water.	Argon and nitrogen in 100 vols. firedamp.	Argon in 100 vols. firedamp.	Argon in 100 vols. nitrogen and argon.
Anzin	400	18·1	0·594	3·28
Bességes	4 to 5	3·8	0·064	1·63
Firminy	16	0·74	0·012	1·67
Liévin	70	8·0	0·166	2·22
Plat-de-Gier	75	30·0	0·601	1·83
Ronchamp	8	2·8	0·031	1·09
Saint-Étienne	600	3·2	0·037	1·17

In the mines of Rochebelle there are sudden, and often violent, outbursts of gas which has the composition CO_2, 98·13, nitrogen

and argon 1·14, methane 0·73. 100 c.c of the gas contains 0·021 c.c. of argon and 100 c.c. of the nitrogen and argon contain 1·87 c.c of the latter.

Argon was found in all specimens of firedamp that were examined, but the proportion of nitrogen and argon in the gas varied widely. The ratio of argon to nitrogen also varied considerably, and often exceeded the ratio in atmospheric air. The most probable explanation is that the argon has been derived not directly from the atmosphere but from air dissolved in water. The possibility of some subterranean source of argon is of course not excluded. C. H. B.

Trinidad Pitch. By STEPHAN F. PECKHAM and LAURA A. LINTON (*Amer. J. Sci.*, 1896, [4], 1, 193—207).—The authors have made analyses of the pitch found in and near the Pitch Lake of the Island of Trinidad. The pitch found within the Lake and also that outside have very much the same composition, and in all cases the pitch is fully saturated with moisture, usually containing some 25 to 30 per cent. About 38 per cent. of the residue is sand, the rest is bitumen and fragments of vegetation and disorganised cellular tissue. The pitch which rises in the middle of the Lake has a vesicular structure. When freshly dug, its colour is brown, but if left in the sun it soon darkens, finally becoming bluish black. A large mass when placed in bright sunshine will melt to a thin pellicle upon the exposed surface and retain the larger part of the water at a temperature sufficient to remove every trace of water if it were dried in the shade. Numerous analyses are quoted. J. J. S.

Rutile, Cassiterite and Zircon. By HERMANN TRAUBE (*Jahrb. f. Min.*, 1896, *Beilage*, *Bd.* 10, 470—476).—By the action of potassium fluoride or of hydrogen potassium fluoride similar etch figures, indicating holohedral symmetry, were obtained on rutile, cassiterite and zircon ; this similarity cannot, however, be taken to support the view that zircon is isomorphous with the other minerals.

Various analyses of rutile have shown small quantities of Fe_2O_3 (up to 10 per cent.), Mn_2O_3 and Cr_2O_3 ; and the author has artificially prepared rutile containing these oxides. By heating titanium dioxide with sodium tungstate and various oxides at a high temperature (1700°) rutile crystals were obtained which contain up to 5·4 per cent. Fe_2O_3, 3·01 Mn_2O_3 or 1.91 Cr_2O_3. Under the microscope, these crystals, as well as the natural crystals, do not show any inclosures, so that these oxides have been dissolved in the titanium dioxide. Cobalt and nickel oxides were not taken up in this way. A peach-coloured cassiterite containing chromium was also prepared.

The changes in colour which occur when crystals of rutile and cassiterite are heated are described, Rutile and cassiterite are acted on by potassium fluoride with the formation of K_2TiO_6 and K_2SnO_6. L. J. S.

Reniform Limestone from Villejuif. By LOUIS FRANCHET (*Bull. Soc. Philomathique, Paris,* 1896, [8], 8, 10—12).—In the limestone at Villejuif are numerous reniform and globular masses very like the menilite of Menilmontant in appearance, and in fact they have

been described as such. The material is white or yellowish and very fine in grain. Sp. gr. 2·34—2·72; H. 4·5—5. Acid dissolves calcium carbonate and leaves a residue of silica. The following analyses show that the material is a siliceous limestone and not menilite, which is a variety of opal.

SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	SrO.	MgO.	K_2O.	Na_2O.	CO_2.	Total.
36·52	1·31	0·23	32·19	0·34	1·69	0·25	0·38	27·81	100 72
24·16	1·53	0·21	38·22	0·42	2·01	0·23	0·44	32·84	100·06

Also traces of manganese and sulphuric acid. L. J. S.

Northupite, Pirssonite, Gaylussite and Hanksite from Borax Lake, California. By JULIUS H. PRATT (*Amer. J. Sci.*, 1896 [4], 2, 123—135).—The minerals here described are found associated with borax at Borax Lake, San Bernardino Co., California. Borax Lake is an alkali marsh which is usually dry, but some water collects in it during the wet seasons.

Northupite (compare Abstr., 1896, ii, 184).—This was found in a single boring as isolated and unmodified regular octahedra. When pure it is colourless, but owing to impurities, probably of clay and organic matter, the colour usually varies from dirty white to dark brown. It is very brittle and shows no cleavage. Sp. gr. 2·380. It is isotropic, and for sodium light μ = 1·5144. The mean of two analyses is

CO_2.	Cl.	SO_3.	MgO.	Na_2O.	K_2O.	H_2O.	Insol.	Total (less O for Cl).
35·12	14·10	0·08	16·08	36·99	Nil	0·72	0·22	100·15

This agrees with the formula $MgCO_3,Na_2CO_3,NaCl$. Cold water acts slowly on the mineral, but hot water decomposes it rapidly with separation of magnesium carbonate. It does not decompose on exposure to air. Fusible at 1 (Kobell's scale), with evolution of carbonic anhydride, and leaving an alkaline mass. [For artificial northupite see Abstr., 1896, ii, 610].

Pirssonite.—This new mineral was found by C. H. Northup as isolated crystals in the same boring as the northupite. The crystals are orthorhombic and hemimorphic; $a : b : c$ = 0·56615 : 1 : 0·3019. The form $e\{131\}$ is present at one end only of the crystals, this being the pyroelectric analogous pole. The mineral is colourless to white, but is often darkened by impurities; it is brittle, and does not show any cleavage. Sp .gr. 2·352; H. 3—3·5. The optical characters are given in detail; with an increase in temperature, there is a small decrease in the value of the optic axial angle. The mean of two analyses is

CO_2.	CaO.	Na_2O.	K_2O.	H_2O.	Al_2O_3, &c.	SiO_2.	Total.
36·07	23·38	25·70	0·15	14·73	0·13	0·29	100·45

Formula, $CaCO_3,Na_2CO_3,2H_2O$; this is like gaylussite, which has, however, $5H_2O$; the two minerals are also somewhat similar in appearance. Practically all the water is expelled below 150.° Before the blowpipe, the mineral decrepitates and fuses at 2—2·5 (Kobell's scale) to an akaline mass. The name is given after L. V. Pirsson.

Gaylussite.—Crystallographic and complete optical determinations have been made on very pure crystals. Sp. gr. 1·992.

Hanksite.—The refractive indices for sodium light are given as $\omega = 1·4807$, $\epsilon = 1·4614$. The usually accepted formula for this mineral is $4Na_2SO_4,Na_2CO_3$; and the potassium and chlorine shown in the two previous analyses have been considered as impurities (salt and sylvite). The author, however, finds that chlorine is present in all crystals, and that microscopical examination shows the presence of only slight impurities. The following analyses have been made on pure material; I, on tabular crystals, and II, on prismatic crystals.

	SO_3.	CO_2.	Na_2O.	Cl.	K.	Insol.	Sp. gr.
I.	45·93	5·65	43·35	2·21	2·48	0·19	2·567—2·553
II.	45·78	5·63	43·61	2·28	2·39	0·12	2·545

The close agreement of both these with previous analyses indicates that chlorine and potassium are not accidental. The formula is now given as $9Na_2SO_4$, $2Na_2CO_3$, KCl. Potassium and sodium do not seem to be isomorphous here, for there is just enough potassium to form potassium chloride. Few minerals contain three acid radicles, as this does. L. J. S.

Mysorine (Anhydrous Copper Carbonate). By LOUIS FRANCHET (*Bull. Soc. Philomathique, Paris*, 1894, [8], 6, 61—65).—Thomson's mysorine from Mysore, although no water is shown in his analysis, has usually been considered to be an impure malachite. In the present paper, material which probably came from the Urals is described. It is amorphous and compact, of a greenish-grey colour, and contains specks of malachite and iron oxide; fracture conchoidal; lustre slightly resinous; sp. gr. 4·398, H. 5·5. Excepting the sp. gr., these characters agree completely with those given by Thomson. The material dissolves in hydrochloric acid with effervescence and separation of sulphur and iron oxide. Analysis gave

CO_2.	CuO (combined with CO_2).	CuO (combined with S).	S.	Al_2O_3.	Fe_2O_3.	SiO_2.	Loss on ignition.	Total.
15·73	56·50	15·67	3·95	2·28	4·90	0·09	0·56	99·68.

This corresponds with 72·23 per cent. of copper carbonate and 19·62 per cent. of copper sulphide. The loss on ignition probably represents the water contained in the small amount of malachite present. Beudant has stated that when malachite is gently heated it loses water and leaves a product having the characters of mysorine; the author has, however, been only able to obtain friable, black copper oxide, as the water and carbonic anhydride are expelled together. Mysorine appears to be a definite mineral species quite distinct from malachite. L. J. S.

A Green Mineral from Brisbane, Queensland. By HENRY G. STOKES (*Proc. Roy. Soc. Queensland*, 1894, 10, 11—13)—Lining joints and cavities in the schists of Adelaide Street, Brisbane, is an amorphous, compact mineral of an apple-green to dark sea-green

colour. It sometimes shows a mammillated surface, and is often streaked with white. Brittle; smooth sub-conchoidal fracture. Thin splinters are sub-translucent. Hardness, 4—5; sp. gr. 2·6. On exposure to air, it decomposes to a white powder. It is infusible, and is slightly attacked by acids. Analysis by E. Hall gave

P_2O_5.	Al_2O_3.	V.	H_2O (loss on ignition).	Total.
48·25	29·07	trace	23·61	100·93

This corresponds approximately with $4Al_2O_3,5P_2O_5,18H_2O$. The colour appears to be due to vanadium. The mineral somewhat resembles turquoise. L. J. S.

Wardite, a new hydrous basic Aluminium Phosphate. By John M. Davison (*Amer. J. Sci.*, 1896, [4], 2, 154—155).—Occasionally, the decomposition of the variscite from Utah (Abstr., 1894, ii, 321) has given rise to cavities in the nodules; wardite incrusts these cavities. It is light-green or bluish-green, with a vitreous lustre, and is concretionary, sometimes approaching to oolitic, in structure. Sp. gr. 2·77; H. about 5, being a little harder than variscite. Analysis gave

P_2O_5.	FeO.	CuO.	MgO.	Na_2O.	K_2O.	H_2O.	Al_2O_3 [diff.].
34·46	0·76	0·04	2·40	5·98	0·24	17·87	[38·25]

Formula: P_2O_5, $2Al_2O_3$, $4H_2O = Al_2(OH)_3PO_4 + \frac{1}{2}H_2O$; or, perhaps, $AlNaPO_4$, $Al(OH)_3 + \frac{1}{2}H_2O$. The following series is made out.

Peganite	$Al_2(OH)_3PO_4 + 1\frac{1}{2}H_2O$
Turquoise	$Al_2(OH)_3PO_4 + 1\ H_2O$
Wardite	$Al_2(OH)_3PO_4 + \frac{1}{2}H_2O$

Before the blowpipe, the mineral swells up and turns white. It is only partially decomposed by acids; hot aqua regia leaves 20 per cent. undissolved, this is, however, soluble after being ignited. When first ignited, about 11 per cent. is insoluble in acids. The name is given after H. A. Ward.

Analyses of the *variscite* agree with that of Packard (Abstr., 1894, ii, 321), but, contrary to his statement, this mineral is completely soluble in aqua regia and in sulphuric acid. At 100—130° it gives off 22·22 per cent. of water, and on ignition 0·50 per cent. more. A pure white variscite from this locality is mentioned, the usual colour being green. L. J. S.

Crocoite from Tasmania. By Charles Palache (*Amer. J. Sci.*, 1896, [4], 1, 389—390).—A crystallographic description is given of crocoite from the silver-bearing lead deposits of Adelaide mine on Mount Dundas, west coast of Tasmania. The light hyacinth-red crystals rest on a matrix of lamellar limonite; they are prismatic in habit, and are translucent with adamantine lustre (compare Abstr., 1896, ii, 657). L. J. S.

Constitution of the Silicates. By Frank W. Clarke (*Bull. U.S. Geol. Survey*, 1895, No. 125, 1—109. Compare Abstr., 1888, 659; 1891, 529).—The author here summarises his views on the constitution of the

naturally occurring silicates and their relations to one another, and in a complete and connected account of the whole series discusses each species in detail. Even when the empirical formulæ have been definitely determined, which, owing to impure material, isomorphous replacements, and defective analyses, has not yet been done in very many cases, there is no method of determining molecular weights, so that attempts to arrive at the constitution of the silicates must be more or less speculative. Simplicity of structure is, however, to be inferred from the occurrence of only a limited number of definite minerals, which are usually exceedingly stable salts and have been formed under special conditions. Of importance in showing the relation in structure of one mineral to others is the study of its alteration products, as shown by pseudomorphs and by such experiments as those of Lemberg, Friedel and others.

All the silicates are considered as salts of one or other of the following silicic acids :—Ortho-, H_4SiO_4 ; meta-, H_2SiO_3 ; diortho-, $H_6Si_2O_7$; dimeta-, $H_2Si_2O_5$; tri-, $H_4Si_3O_8$. Besides normal salts, there are also double salts, and basic and acid salts, and it is often impossible to distinguish between these ; for example, Al_2SiO_5 may be expressed as a basic metasilicate by three different structural formulæ, or as an orthosilicate by two. A large number of minerals may be most easily interpreted as orthosilicates, and, most of these being salts of aluminium, they can be considered as substitution derivatives of the normal salt, $Al_4(SiO_4)_3$, which is taken to be a fundamental molecule in this theory of the silicates. This salt, which is possibly represented by the mineral xenolite, can be written structurally in several different ways ; the one here adopted is $Al\vdots[(SiO_4)\vdots Al]_3$. The following groups are then made out, and, under the various heads, the constitution and relations of all known silicates which can be referred to mineral species are minutely discussed.

Orthosilicates of aluminium.—I. The nephelite type.—Here one atom of aluminium is replaced by R'_3 ; for example, nephelite, $Al_3(SiO_4)_3Na_3$; muscovite, $Al_3(SiO_4)_3KH_2$; topaz, $Al_3(SiO_4)_3(AlF_2)_3$; andalusite, $Al_3(SiO_4)_3(AlO)_3$. This brings out the relation between topaz and andalusite, and their alteration to muscovite.

II. The garnet-biotite type.—Here the general formula is $Al_2(SiO_4)_3R'_6$. Of the three subtypes, the first includes natrolite, $Al_2(SiO_4)_3Na_2H_4$; the second biotite, $Al_2(SiO_4)_3Mg_2HK$; and the third the garnets, $R'''_2(SiO_4)_3R''_3$, and the epidote group, $R'''_2(SiO_4)_3R''_2(R'''OH)$. The relations between garnet, epidote and idocrase are discussed. Sodalite, $Al_2(SiO_4)_3Na_4(AlCl)$, and cancrinite, $Al_2(SiO_4)_3Na_4H(AlCO_3)$, are placed in this group.

III. The felspars and scapolites.—There is a parallelism between these two series, and both yield muscovite and kaolin as alteration products. The end members of the series are expressed as : albite, $Al(Si_3O_8)_3Na_3Al_2$; anorthite, $[Al(SiO_4)_3Al_2Ca]_2Ca$; marialite, $Al(Si_3O_8)_3Na_4Al(AlCl)$; meionite, $[Al(SiO_4)_3Al_2Ca]_2Ca_2O$. Kaolin is given as $OH\cdot Al(SiO_4)_2AlH_3$. Leucite is related to the feslpars and garnets, and is written as a pseudometasilicate, $Al(Si_3O_8)_2(SiO_4)_2K_4Al_3$.

IV. The normal zeolites.—These are related to nephelite and the felspars, and may be called felspathic zeolites (Abstr., 1894, ii, 459).

V. The micas and chlorites.—(Abstr., 1890, 460; 1892, 125, 794; 1893, ii, 78; 1896, ii, 37.)

VI. The tourmaline group.—Four types of tourmaline are given, and are written as two $Al(SiO_4)_3R'''_2(Al{\cdot}BO_2)$ groups connected by $Al(BO_3)NaH$, where R''' is Al, R'_3 or MgH; this formula explains the alteration of tourmaline to mica. Axinite and some other borosilicates are considered here.

VII. Miscellaneous species.—For staurolite is suggested

$$[Al(SiO_4)_3(AlO)_6Fe]_2Fe.$$

Orthosilicates of the Dyad Bases.—It is here necessary in most cases to assume polymerisation; for example, the members of the humite group, as recently shown by Penfield and Howe, are derivatives of the salts $Mg_8(SiO_4)_4$, $Mg_6(SiO_4)_3$, and $Mg_4(SiO_4)_2$. And owing to the existence of trimerite, $Be_3Mn_2Ca(SiO_4)_3$, phenakite is written with the triple formula $Be_6(SiO_4)_3$. The constitution of serpentine is discussed, and is expressed as $H_3(MgOH)Mg_2(SiO_4)_2$. The structural formulæ of these are written as rings or series of rings, others are written as open chains, for example, dioptase, $Cu_3(SiO_4)_4H_8Cu$.

Orthosilicates of Tetrad Bases.—To zircon is given the polymeric expression $Zr(SiO_4)_4Zr_3$, and from this other zirconium silicates are derived. Auerbachite is $Zr_4(Si_3O_8)(SiO_4)_3$; and eudialyte and eucolite are mixtures of tri- and orthosilicates forming a group like the felspars. Thorium and titanium silicates find a place here.

Diorthosilicates.—Although ethereal salts of $H_6Si_2O_7$ are known, the metallic salts are uncertain. The typical member of the group is barysilite, $Pb_3Si_2O_7$, and other lead silicates belong here. Apophyllite is given as $Ca_2(Si_2O_7)_3H_{12}(CaOH)_2$, and to it okenite and gyrolite are related. Cordierite seems to be the only aluminium salt.

Meta- and Dimetasilicates.—These are not easy to interpret, and in the case of the pyroxenes and amphiboles the analyses show variations from the metasilicate ratio. Wollastonite and pectolite are given as $Ca_2(SiO_3)_3Ca$ and $Ca_2(SiO_3)_3NaH$ respectively, as being chemically dissimilar from the normal pyroxenes. The fact that spodumene splits up on alteration into eucryptite and albite suggests that it is a mixed ortho- and tri-salt, to be written as $Al_6(Si_3O_8)_3(SiO_4)_3Li_6$; by analogy the other pyroxenes are also written as pseudometasilicates, $R''_8(Si_3O_8)_2(SiO_4)_2$; and Tschermak's aluminous constituent of augite is taken six times as $Al_6(SiO_4)_3(SiO_4)_3(AlO_2Mg)_6$. As the amphiboles have a less specific gravity than the pyroxenes, they may be supposed to have smaller molecules (this is opposed to the usually accepted formulæ $CaMgSi_2O_8$ and $CaMg_3Si_4O_{12}$ of diopside and tremolite respectively), and, considering them as pseudometasilicates with the bases replaceable by fourths, the formula may be written as $R''_4(SiO_4)(Si_3O_8)$; glaucophane is $Mg_2Na_2(AlO)_2(Si_3O_8)_2$. The pyroxenes are then bipolymerides of the amphiboles, and the character of the structure is the same for both groups.

Petalite, $AlLi(Si_2O_5)_2$, and milarite, $HKCa_2Al_2(Si_2O_5)_6$, are dimetasilicates, and so are mordenite and ptilolite (Abstr., 1893, ii, 77).

L. J. S.

Microcline from the Spessart. By E. PHILIPPI (*Ber. Senckenb. Ges. Frankfurt*, 1896, 125—133).—In the gneiss of the Spessart Mountains near Damm and Aschaffenburg are pegmatite veins containing pale flesh-red felspar. The cleavage angle, 001 : 010, of this felspar varies from 90° 1′ to 90° 11′; macroscopically, no albite lamellæ are seen. As shown by micro-chemical reactions, the small amount of soda varies in quantity, and, for the following analysis, a specimen containing apparently the average amount was selected.

SiO_2.	Al_2O_3.	Fe_2O_3.	CaO	MgO.	K_2O.	Na_2O.	Loss on ignition.	Total.
63·84	19·74	0·03	0·21	0·06	13·42	1·82	0·39	99·51.

Sp. gr. 2·562. The amount of calcium corresponds with 1·10 per cent. of anorthite, and the sodium with 15·75 per cent. of albite. After deducting this plagioclase material, and calculating the remaining silica, alumina, and potash to 100, the composition of the potash felspar is SiO_2 63·84, Al_2O_3 19·85, K_2O 16·31; here there is an excess of 1·42 per cent. of alumina over the theoretical amount, which indicates commencing alteration, a fact also shown by the microscopical examination.

The angle of optical extinction on *b*(010) is 5—7°, as in orthoclase; on *c*(001), it varies from 2° to 16°. The mineral is a microcline-perthite, with albite lamellæ usually in one direction only; the microscopical characters of these lamellæ are described in detail.

L. J. S.

Rocks and Asbestos from Corsica. By M. OELS (*Jahrb. f. Min.*, 1896, i, Ref., 46; from *Inaug.-Diss. Erlangen*, 1894).—Actinolite-asbestos from Luri and Morosaglia, Corsica, gave the following results on analysis.

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MgO.	CaO.	H_2O.	Total.	Sp. gr.
55·65	1·73	2·45	0·13	23·56	14·64	0·98	99·14	2·99
56·84	2·64	1·05	0·36	24·05	14·18	1·89	101·01	3·09

Several analyses of serpentine, as well as of some other rocks, are given.

L. J. S.

Pyrophyllite from the Urals. By FRANZ LOEWINSON-LESSING (*Verh. russ.-k. min. Ges.*, 1895, [2], **33**, 283—287).—The pyrophyllite occurring in radial aggregates at Pychminsk, near Beresovsk, is shown to consist of a mechanical mixture of two minerals which may be separated by means of Thoulet's solution. The heavier portion gave analysis I, this corresponding with $3H_2O,3Al_2O_3,11SiO_2$, and so being near to the formula usually given for pyrophyllite, namely,

$$H_2O,Al_2O_3,4SiO_2;$$

the lighter portion gave analysis II., this corresponding with $3RO,8H_2O,4Al_2O_3,9SiO_2$, and is therefore distinct from pyrophyllite,

which it closely resembles in appearance; the name *pseudopyrophyllite* is given to this lighter mineral.

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MgO.	CaO.	Loss on ignition.	Total.	Sp. gr.
I.	64·94	29·22	—	—	0·16	0·67	5·90	100·89	2·782
II.	43·68	32·60	3·13	0·30	9·08	0·59	11·52	100·90	2·687

Hermann's analysis of the Pychminsk mineral agrees fairly closely with a mixture of three parts of pyrophyllite and one of pseudopyrophyllite. The pseudopyrophyllite is harder, and greener in colour than the pyrophyllite; both are orthorhombic, with a very perfect basal cleavage; the acute optical bisectrix is perpendicular to the cleavage, and the dispersion of the axes is feeble with $\rho > v$. Pseudopyrophyllite differs from pyrophyllite in having a larger optic axial angle, and in being optically positive. The microscopical examination points to a variability in the composition of pseudopyrophyllite.

L. J. S.

A Crystal of Labradorite from Gabbro. By N. H. WINCHELL (*Bull. Mus. Hist. Nat.* (*Paris*), 1896, 160—161).—Blocks of gabbro from Bearev Bay, Minnesota (N.E. shore of Lake Superior), contain large crystals of labradorite; one of these crystals is described. Optical extinction angle on *b* (010) 25—27°, on *c* (001) 7—11°; sp. gr. 2·72. Analysis gave

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	K_2O.	Na_2O.	Total.
50·75	32·80	0·22	—	13·69	0·04	0·12	2·60	100·22.

This is between $Ab_1\ An_2$ and $Ab_1\ An_3$, and corresponds with labradorite-bytownite.

L. J. S.

Alteration of Glauconite. By K. D. GLINKA (*Annuaire Géol. Min. de la Russie*, 1896, **1**, Mem. 1—3).—Gümbel has stated that glauconite alters to limonite, and Koudriavtseff gives silica as an alteration product of this mineral. It is pointed out that mineral waters from glauconite rocks contain iron and potassium, and the hydrated iron oxides which cement these rocks have probably been derived from the glauconite. Analyses of the altered mineral show that with a decrease in the iron and potassium there is an increase in the aluminium, the end product then being a ferruginous clay. Reasons are given for doubting Koudriavtseff's conclusion that silica is an end product.

L. J. S.

Artificial Production of Rocks by Fusion in the Presence of Various Agents. By CORNELIUS DOELTER (*Jahrb. f. Min.*, 1896, i, 211—212). K. Schmutz, under the direction of the author, has fused natural rocks in the presence of various agents; the fused products consist of a glassy base containing the minerals mentioned below. When eclogite was fused with calcium and sodium fluorides, the resulting glass contained meionite and plagioclase. Leucitite with calcium chloride gave orthoclase; with sodium fluoride and potassium silicofluoride, it gave scapolite, mica and magnetite; and with sodium chloride the same rock gave augite, scapolite and magnetite. Granite

with sodium chloride and potassium tungstate gave plagioclase, augite, and tridymite; in the presence of other agents, olivine, augite or scapolite accompanied the plagioclase. Nephelite-basalt with calcium fluoride, sodium chloride and boric acid gave magnetite, anorthite and augite. A chlorite-schist containing pyrites when fused with sodium and aluminium chlorides gave oligoclase, mica, pyrites, and haüyne. L. J. S.

Analcite Diabase from California. By HAROLD W. FAIRBANKS. (*Jahrb. f. Min.*, 1896, ii, Ref., 89—90; from *Bull. Dept. Geol. Univ. California*, 1895, **1**, 273—300).—In San Luis, Obispo Co., California, are three isolated occurrences of analcite-diabase in large dykes; these rocks are interesting on account of their relations to teschenite and theralite. The rock of the most important of these, the Cuyamas dyke, is much decomposed, and contains, in order of formation, magnetite, olivine, a plagioclase near labradorite, augite, and analcite; the structure is granular. Intersecting the main dyke are numerous smaller dykes, in which the rock is fresh and contains the same minerals as before, with the exception of olivine; here the structure is panidiomorphic. The analcite occurs under four different conditions: (1) lining cavities, (2) filling angular spaces between the felspar crystals, (3) replacing felspars, (4) in one of the dykes in the form of hexagonal or rounded grains partly enclosed within the felspars; it is considered to be an alteration product of nephelite. Secondary felspar and prehnite replace analcite. Analysis by V. Lenher of the rock from one of the secondary dykes gave—

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	K_2O.	Na_2O.	H_2O.	Cl.	Total.
50·55	20·48	2·66	4·02	7·30	4·24	2·27	8·37	0·44	trace	100·33

L. J. S.

Comendite, a new Rhyolite. By S. BERTOLIO (*Jahrb. f. Min.*, 1896, ii, Ref., 76—77; from *Rend. Accad. Lincei*, 1895 [5], **4**, Sem. 2, 48—50).—The island of S. Pietro, off the west coast of Sardinia, consists of very acid volcanic rocks; these are liparites rich in alkalis, and containing much quartz and chalcedony. Basic minerals are subordinate; biotite and hornblende occur in some of the rocks, but more usual is a pyroxene resembling ægyrite, which shows the pleochroism $\mathfrak{c}$ bright yellow, $\mathfrak{b}$ green-yellow, $\mathfrak{a}$ leaf-green. Liparites with an alkali pyroxene form a new group, to which the name *comendite*, from the locality Comende, is given. The rock also contains an amphibole resembling arfvedsonite, with pleochroism $\mathfrak{c}$ brown, $\mathfrak{a}$ greenish-yellow. In a previous paper (*Boll. Com. Geol. Ital.*, 1894, **25**, 407), the author gives the following analysis of this rock.

SiO_2.	Al_2O_3,Fe_2O_3.	CaO.	MgO.	K_2O.	Na_2O.	Total.
80·3	9·2	trace	0·6	3·9	5·5	99·5.

L. J. S.

Green Slate from Llanberis. By JOHN H. COSTE (*Ber.*, 1896, **29**, 2450—2451).—Green slate from the Dinornwig quarry near Llanberis gave the following results on analysis: the composition is

similar to that of a clayey soil. The portion soluble in strong hydrochloric acid gave I, and the insoluble portion II.

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	Not det.
I.	—	4·79	1·52	3·96	0·22	2·14	—
II.	77·37	18·68	1·60	—	trace	—	2·35

	Na_2O, K_2O.	P_2O_5.	Insol.	Loss on ignition.	Total.
I.	0·13	0·41	85·06	1·34	99·57

The presence of phosphoric acid is noteworthy. Seminormal hydrochloric acid acts appreciably on the rock, and extracts 0·089 per cent. of phosphoric acid. Sp. gr. of the rock = 2·818. L. J. S.

Theralite from Costa Rica. By JOHN E. WOLFF (*Amer. J. Sci.*, 1896, [4], 1, 271—272).—This rock forms a large intrusion in Tertiary limestone on the Atlantic slope of the Costa Rica volcanic plateau. It is a dark grey spotted rock, and shows distinct crystals of augite and biotite, and rounded areas of radiated zeolites. The microscope shows: augite, plagioclase (labradorite), sanidine, nephelite, a mineral of the sodalite group, olivine, biotite, magnetite, apatite, and analcite and other zeolites. The main differences from the Montana type are the absence of ægyrite, the distinctly basic plagioclase, and the small amount of sanidine; it is also probably poorer in alkalis. This is the nearest approach yet described to the theralite of Rosenbusch, namely, a plutonic plagioclase-nephelite rock. L. J. S.

Altered Vesuvian Lava. By FRANZ LOEWINSON-LESSING (*Annuaire Géol. Min. de la Russie*, 1896, 1, Section II, 10—11; from *C. R. Soc. Naturalistes St. Petersbourg*, 1895, No. 1, 15—16).—A lava stream of 1631 forms a sea-cliff at La Scala in the harbour of Resina; the long action of a warm saline solution in the form of spray has decomposed the rock to a soft, friable mass containing porphyritic crystals of augite and leucite. Analysis of this decomposed rock gave the results under I; this is compared with the average composition of Vesuvian lava II.

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	Na_2O.	K_2O.	Loss on ignition.	Total.
I.	48·31	24·23			9·54	8·24	4·83	2·77	1·73	99·65
II.	47·82	18·85	5·24	5·12	9·51	4·40	2·65	6·41	—	100·00

This shows that ferrous iron and potash have been replaced by magnesia and soda respectively. The material contains 1·32—1·55 per cent. of chlorine, which can be extracted by water as chlorides of sodium and magnesium. L. J. S.

Meteoric Irons—[Rhabdite and Schreibersite]. By EMIL W. COHEN (*Jahrb. f. Min.*, 1896, ii, Ref., 42—43; from *Ann. k.k. Naturhist. Hofmuseums, Wien*, 1894, 9, 97—118).—In No. III. of his "Meteoric Iron Studies" the author gives analyses of several irons, and of the isolated rhabdite needles. It is shown that the acicular rhabdite and

the platy schreibersite have the same chemical composition, namely, $(Fe,Ni,Co)_3P$; the two occur together and only differ in habit. Goniometric measurements of rhabdite needles showed the existence of a tetragonal prism zone. The irons examined were :—I See-Läsgen, Prussia; II Bolson de Mapimi [= Coahuila], Mexico; III Sanchez Estate, Mexico; IV Hex River Mounts, S. Africa; V Schwetz, Prussia; VI Rasgata, New Granada; VII Lime Creek [=Claiborne], Alabama. The mineralogical composition of these is as follows.

	I	II	III	IV	V	VI	VII
Nickel iron	98·76	98·344	98·49	97·99	98·55	97·10	96·96
Ni-Fe phosphides	1·21	1·615	1·49	1·97	0·17	1·73	2·91
Carbon	0·01	0·011	0·02	0·02	0·01	0·07	0·01
Chromite and silicates	0·01	0·003		0·02	0·02	0·03	0·09
Daubréelite	0·01	0·027	—		—	—	0·03
Tænite	—	—	—	—	0·89	0·15	—
Angular fragments	—	—	—	—	0·36	0·56	—
Insoluble	—	—	—	—	—	0·36	—

The action of acid on the different irons of similar chemical composition is very variable, dissolution taking place in a few days, or only after an interval of months. Analysis of the portions soluble in dilute hydrochloric acid gave

	Fe.	Ni.	Co.	P.	Cu.
I	92·23	7·24	0·47	0·04	0·02
II	94·22	5·17	0·54	0·06	0·01
III	92·47	6·68	0·53	0·0469	0·0148
VI	92·29	5·50	0·84	0·15	0·02
VII	93·86	4·97	0·76	0·16	0·01

Analysis of the isolated rhabdite needles gave

	Fe.	Ni.	Co.	P.	Cr.	S (calcd.)	Residue.	Total.
I	49·06	35·48	0·45	13·35	0·48	0·58	0·63	100 03
II	51·60	30·89	0·70	14·63	0·78	—	0·96	99·56
III	55·01	28·63	0·60	15·24	0·43	—	—	100·19
IV	55·54	26·73	0·46	15·10	0·25	0·30	—	98·91
VII	47·22	30·16	0·38	14·16	0·95	1·16	—	95·57

With III, there is 0·28 per cent. of carbon; in IV and VII are small quantities of chromite and silicates.

Analysis of schreibersite from IV gave

Fe.	Ni.	Co.	P.	Cr.	Chromite.	S.	Total.
61·46	21·31	0·34	15·20	0·32	0·25	0·39	99·27

L. J. S.

The Meteorite of Hamblen Co., Tennessee. By GEORGE P. MERRILL (*Amer. J. Sci.*, 1896, [4], 2, 149—153).—Eakins's analyses of this meteorite (Abstr., 1894, ii, 56) showed that olivine could be present in only small quantities, for in the 37·63 per cent. of the stony portion which was soluble in hydrochloric acid only 1·34 per cent. of magnesia was present; and at the time no satisfactory conclusion was come to as to the mineral composition, beyond that the insoluble portion consisted mainly of pyroxene.

Microscopical examination by the present author shows a holocrystalline, granular ground-mass of enstatite, diallage, and anorthite, with porphyritic pyroxenes and some indeterminable material between the grains. Olivine is inconspicuous, and cannot be separated. The anorthite gave the following results on analysis.

SiO_2.	Al_2O_3.	FeO.	CaO.	MgO.	Na_2O.	Total.
42·02	37·77	trace	16·41	0·96	not det.	97·16

The enstatite was found to contain magnesium, but no calcium or aluminium. These minerals do not, however, altogether satisfy the requirements of the analysis of the soluble portion. After separating the anorthite as far as possible, some of the material is still gelatinised by acid, and, as magnesium and calcium go into solution, the presence of monticellite is suggested. When the stony portion of the meteorite is boiled with water, chlorine, sulphuric acid, calcium and iron are extracted; this suggests the presence of gypsum (derived from oldhamite) and lawrencite. The minerals probably present are then: nickel-iron, enstatite, diallage, anorthite, olivine (or monticellite), oldhamite (or secondary gypsum), lawrencite, troilite, and schreibersite.

The meteorite is to be classed as a mesosiderite; but the composition and structure are very variable, for the stony and metallic portions each in turn predominate in different parts. In the coarser portions, especially when near the metallic iron, there is a strongly marked cataclastic structure, which is well shown in the anorthite. The average sp. gr. of the fragments is 4·32.

[Eakins in a later note (*Amer. J. Sci.*, 1893, **46**, 482) had corrected some errors in his formula, and suggested that the soluble portion might consist of olivine and anorthite.] L. J. S.

The Geologic Efficacy of Alkali Carbonate Solutions. By EUGEN W. HILGARD (*Amer. J. Sci.*, 1896, [4], 2, 100—107. Compare Abstr., 1893, ii, 165).—The presence of alkali carbonates in mineral waters is usually explained by supposing that carbonic anhydride has extracted the alkalis from silicates; but it is better explained by the fact that alkali carbonates are formed when a solution of an alkali sulphate or chloride is treated with calcium or magnesium carbonate in the presence of carbonic anhydride. The action of alkali carbonates in soils and in hardening muds is discussed, as is their efficacy in the alteration and metamorphism of rocks, and in the formation of mineral veins. L. J. S.

Artesian Waters of N. S. Wales. By JOHN C. H. MINGAYE (*Australian Assoc. Adv. Sci.*, 1895, 6, 265—277).—Nineteen analyses are given of the water from artesian bores in the western district of

New South Wales; the total solids, except in five cases, are small, and consist mainly of sodium and potassium carbonates, and sodium chloride, with less calcium and magnesium carbonates, alumina, silica, and organic matter. The value of these waters for irrigation and other purposes is discussed. Analyses of the soluble salts in two samples of soils are given. The deteriorating action on plants of alkali carbonates introduced by irrigation may be counteracted by gypsum. L. J. S.

Physiological Chemistry.

Oxygen Tension of Arterial Blood. By JOHN S. HALDANE and J. LORRAIN SMITH (*J. Physiol.*, 1896, **20**, 497—520).—The aërotometric method of estimating the oxygen tension in blood is open to many objections that are pointed out. The value of the present method is accentuated by the fact that it is applicable to animals and men during life. The subject breathes air containing a small known amount of carbonic oxide until the percentage saturation of his hæmoglobin with that gas is constant. The final saturation with carbonic oxide of hæmoglobin solutions can be determined with quite small quantities of blood from the finger by a method previously described; it depends on the relative tensions of carbonic oxide and oxygen in the liquid, so that if the tension of carbonic oxide and the final saturation of the hæmoglobin are known, the oxygen tension can be inferred. Full details of the method of titration with carmine and a few necessary corrections are given.

It was proved that the oxygen tension of human arterial blood is 26·2 per cent. of an atmosphere or 200 mm. of mercury; as this is higher than the tension of oxygen in the alveolar air, diffusion alone will not explain the passage of oxygen from the alveolar air to the blood. Carbonic oxide is not oxidised in the body. W. D. H.

Muscular Power and Gaseous Metabolism. By LOUIS SCHNYDER (*Zeits. Biol.*, 1896, **33**, 289—319).—The increased discharge of carbonic anhydride that occurs during work is lessened by practice. The amount of decomposition of tissue depends on the extent of the exertion rather than of the work done. In normal individuals, the involuntary muscles are already in a state of "training," and in weakened convalescents these work with abnormal exertion even during so-called rest. W. D. H.

The Lowest Limit of Nitrogenous Equilibrium. By ERWIN VOIT (*Zeits. Biol.*, 1896, **33**, 333—351).—This paper is principally polemical. In it, with a few new experiments, C. Voit's original teaching is confirmed, and Munk's criticisms on this work combated.

W. D. H.

Influence of Fat on Nitrogenous Metabolism. By A. WICKE and HUGO WEISKE (*Zeits. physiol. Chem.*, 1896, **22**, 265—277. Compare Abstr., 1895, ii, 516; 1896, ii, 198, 535).—This is a continuation of previous work. The general conclusions are that in herbivora (sheep), gradually increasing doses of fat added to a rich proteid diet cause a smaller nitrogenous assimilation, and the output of nitrogen gets less until equilibrium is established. This has a limit which was reached in the authors' experiments when the daily dose of fat amounted to 150 to 180 grams; beyond that, nitrogenous metabolism is increased.

W. D. H.

Preparation of Pepsin. By CORNELIS A. PEKELHARING (*Zeits. physiol. Chem.*, 1896, **22**, 233—244).—A very powerful preparation of pepsin is obtained by dialysing artificial gastric juice against distilled water; the pepsin is precipitated, redissolved in dilute hydrochloric acid, and reprecipitated by dialysis. There is much loss of material in the process. It gives the proteid reactions and contains phosphorus (less than 1 per cent.). This may be in the pepsin or in a nucleo-proteid mixed with the pepsin, but it is not due to admixture with lecithin. By heating a solution, the phosphorus-containing substance is precipitated, and proteose goes into solution. The quantity of phosphorus in this nucleo-proteid is less (0·3 per cent.) than in the original substance; some unknown phosphorus-containing substances passing into solution. The nuclein yields alloxuric bases.

The activity of this pepsin is destroyed by alcohol, or by heating it to the temperature (60—70°) to which the precipitation just described occurs.

If commercial pepsin is digested with 0·3—0·5 per cent. hydrochloric acid, even for 5 days, it still continues to curdle milk. This is contrary to Hammarsten's statement. W. D. H.

Bromine in the Animal Body after the Administration of Bromine Compounds. By WERNER ROSENTHAL (*Zeits. physiol. Chem.*, 1896, **22**, 227—232).—Four dogs were fed on Paal's hydrogenbromide-peptone added to flesh and milk. There were no toxic symptoms. After death, bromine was found in the thyroid (small quantities occur with iodine in the normal thyroid), liver, spleen, hair, pancreas, muscles and kidney in small quantities. About the same quantity is found when potassium bromide is given. W. D. H.

Effects of the Injection of Peptone into the Circulation. By WILLIAM H. THOMPSON (*J. Physiol*, 1896, **20**, 455—473).—In dogs, Witte's "peptone," in doses below 0·02 gram per kilo. of body weight, produces hastening of coagulation; above this dose, it causes retardation, as others have found. In doses as low as 10—15 milligrams per kilo, it causes a fall of blood pressure when the rate of injection is rapid; this is due to vascular dilatation by a direct influence on the blood vessels of the splanchnic and other areas. No indirect influence through the vaso-motor centre was observed, the

results found being practically the same even after severance of the cervical cord. W. D. H.

Action of Carbonic Anhydride on Muscle. By AUGUSTUS D. WALLER and Miss S. C. M. SOWTON (*Proc. Physiol. Soc.*, 1896, 16—17).—In ordinary striped muscle, stimulation in the presence of carbonic anhydride results in the staircase phenomenon. The conclusion is drawn that this phenomenon is due, as in nerve, to the evolution of the gas during contraction. With heart muscle, the effect, however, of stimulation is simply decrease in contraction and electrical response; there is no augmentation or staircase at first. Ether and chloroform act similarly. W. D. H.

Nucleo-proteid in Muscle. By CORNELIS A. PEKELHARING (*Zeits. physiol. Chem.*, 1896, **22**, 245—247).—Whitfield's (Abstr., 1894, ii., 358) failure to obtain nucleo-proteid from muscle is due (1) to the fact that he used water as the extracting agent; this rapidly becomes acid, and nucleo-proteids are insoluble in dilute acids; (2) gastric digestion, if the quantity of nuclein is small and the percentage of hydrochloric acid over 0·1, may not give rise to a precipitation of nuclein. In the present research, the muscles of various animals were used; the extracting agent was 0·25 per cent. solution of sodium carbonate. From the extract, which contains very little myosin, a nucleo-proteid is precipitable by acetic acid, two grams were obtained from 543 grams of flesh; it causes intravascular clotting, and contains 0·7 per cent. of phosphorus; its nuclein contains 3·5 per cent. of phosphorus and yields the alloxuric bases xanthine and guanine in small quantities. W. D. H.

Occurrence of Inosite in the Thyroid Gland. By R. TAMBACH. (*J. Pharm.*, 1896 [6], 4, 119.)—This substance appears to occur in larger quantity, from 0·5 to 0·8 per cent., in the thyroid gland than in any other part of the body. M. W. T.

Chemistry of the Thyroid. By SIGMUND FRÄNKEL (*Wien. med. Blätter*, 1896, Nos. 13, 14, 15).—The paper gives further particulars regarding the metallic compounds of thyreo-antitoxin (Abstr., 1896, ii, 119). A second base was also separated from the proteid free extract of the gland. The gland contains a considerable quantity of inosite. The conclusion of Drechsel and Kocher, that the organ forms more than one physiologically active substance, is supported.

W. D. H.

Chemistry of the Thyroid Gland. By ROBERT HUTCHISON (*J. Physiol.*, 1896, **20**, 474—496).—The thyroid contains two proteids, a nucleo-albumin, and the colloid matter; the former is present in small amount, and is probably derived from the epithelium. It was prepared by Halliburton's sodium chloride method. The colloid is contained in the acini. It contains a small amount of phosphorus and a considerable proportion of iodine; it yields no reducing substance on treatment with mineral acids, and no nuclein bases and is, therefore, neither a mucin, nor a nucleo-proteid. On gastric digestion, it is

readily split into a proteid and a non-proteid part; both of these, but especially the latter, contain iodine. The non-proteid part contains all the phosphorus of the original substance. The ordinary extractives are fairly abundant; but the colloid is the active physiological constituent of the gland; both parts of it are active, but the non-proteid part is the more active of the two. W. D. H.

Chemistry of the Mucin of the Respiratory Tract. By FRIEDRICH MÜLLER (*Centr. Physiol.*, 1896, **10**, 480—481, from *Sitz. Ges. Beförd. Naturw. Marburg*, 1896, No. 6).—The mucin of sputum was prepared by solution in alkali, and precipitation by acid and subsequently by alcohol; it is free from nuclein. After treatment with dilute sulphuric acid, it yields from 25 to 32 per cent. of a reducing substance; this is not a pentose, and the hexose prepared from it could not be identified with any known sugar; probably it may be glucosamine. W. D. H.

The Nucleins of Pus. By EMILE LEIDIÉ (*J. Pharm.*, 1896 [6], **4**, 150—155).—The nucleins appear to be a class of substances which differ widely amongst themselves in composition, and in the manner in which they decompose. This investigation was undertaken for the purpose of comparing the nucleins of purulent urine with those obtained from other sources. A mixture of alkali-albumins and nucleo-albumins was obtained by a method described in another paper (next abstract), and from this a nuclein. The results of the estimation of sulphur, phosphorus, and nitrogen in this substance agreed closely with those obtained by Hoppe-Seyler for a nuclein from another source. M. W. T.

The Proteids of Purulent Urine (Pyin and Mucin). By EMILE LEIDIÉ. (*J. Pharm.*, 1896 [6], **4**, 97—103).—The author considers that the two substances, mucin and pyin, which are usually taken as indicating the presence of pus in urine, are not originally present in the pus, but are produced by the action of alkalis on its constituents. When purulent urine, which has usually a slightly acid character, is preserved from contact with air, the leucocytes remain intact, and the liquid is found to contain neither mucin nor pyin. When the urine undergoes ammoniacal fermentation, the leucocytes quickly break up, and dissolve in the liquid. The liquid now contains both mucin and pyin, which, however, cannot be said to be derived from the broken down leucocytes, as the quantity increases with the duration of fermentation.

Pyin appears to be an alkali-albumin, and the mucin of acid purulent urine a nucleo-albumin, whilst the so-called mucin of the mucus of the bladder is probably a mixture consisting principally of a globulin. M. W. T.

Proteids of Milk and the Methods for their Separation. By A. SCHLOSSMANN (*Zeit. physiol. Chem.*, 1896, **22**, 197—226).—A criticism on the methods at present in use for the separation and estimation of the proteids in milk. A new method is also recommended; it consists in adding to the milk a small quantity of a saturated

solution of potassium alum at 37°. This precipitates the caseinogen in an insoluble form, and leaves the albumin and globulin unprecipitated. This is true for human, cows', asses', and pigs' milk. The globulin is precipitated from the filtrate by magnesium sulphate, and the albumin determined by difference.

In cows' milk, the numbers given are: caseinogen 3·185, globulin 0·154 and albumin 0·374 per cent. The importance of the albumin and globulin in nutrition is insisted upon. W. D. H.

Action of Rennet. By R. BENJAMIN. (*Virchow's Archiv*, 1896. **145**, 30—48).—This work is largely a criticism of Peter's researches (Abstr., 1895, ii, 80. Compare also Hammarsten, Abstr., 1896, i, 583, Edmunds, *ibid.*, ii, 489). The conclusions drawn are that rennet acts only on the caseinogen of milk and on no other proteid of either animal or vegetable origin; solutions of caseinogen fermentable in this way are, like milk itself, alkaline to lacmoid and acid to phenolphthaleïn; a caseinogen solution is only coagulable in the presence of soluble calcium salts. W. D. H.

Estimation of Sulphur in Animal Tissues, and in the Hair of Animals of different Ages. By FRANZ DÜRING. (*Zeits. physiol. Chem.*, 1896, **22**, 281—284).—Sulphur was estimated in the hair of men and animals, in hoofs, and in rabbits' flesh; the method used being a modification of Hoehnel-Glaser's. The results are very close to those of Mohr (Abstr., 1895, i, 255). The percentage of sulphur in rabbits' hairs at different ages was also investigated; the numbers lie between 3·9 and 4·6 per cent., but there is no such marked variation with age as Weiske (*Landw. Versuchs-Stat*, **36**, 81) found in birds' feathers. W. D. H.

Physiological Action of Nitrites. By JOHN S. HALDANE, R. H. MAKGILL and A. E. MAVROGORDATO. (*Proc. Physiol. Soc.*, 1896, 18).—Nitrites convert the hæmoglobin of the blood into a mixture of methæmoglobin and nitric-oxide-hæmoglobin. In excess, amylic nitrite causes the appearance of photomethæmoglobin. Death caused by nitrites is due simply to their action on hæmoglobin. If the oxygen in the blood plasma is simultaneously increased by administration of the gas at high pressure, this is sufficient to support life, in spite of the fact that the hæmoglobin is no longer capable of carrying oxygen. The experiments were made on mice and rabbits, and are similar in plan and results to those previously described in carbonic oxide poisoning (Abstr., 1895, ii, 407, also 1896, ii, 52). W. D. H.

Physiological Action of the Suprarenal Capsules. By SIGMUND FRÄNKEL (*Wien. med. Blätter*, 1896, Nos. 14, 15, 16).—The main action of an extract of the medulla of the suprarenal capsules when injected into the circulation is a rise of blood pressure. This is due to peripheral action on the small vessels, as Schäfer and Oliver (Abstr., 1895, ii, 235) showed; and as Moore (*ibid.*, 236) stated this is due to a reducing substance originally described by Vulpian. The present research is directed to an examination of this substance; this was

separated by extraction with alcohol and acetone, but not crystallised. The name *spygmogenin* is suggested for it. Its chemistry is not yet fully worked out, but its reactions point to its being a nitrogenous derivative of the ortho-dihydroxybenzene series. W. D. H.

The Significance of Chlorides in Anæmia. By WACLAW VON MORACZEWSKI (*Virchow's Archiv*, 1896, **145**, 458—480).—During anæmia, there is a diminution in the excretion of chlorides in the urine; the excretion increases as the patient gets better. Calcium phosphate behaves like the chlorides. The alkali phosphates and uric acid are increased in amount in the urine in the anæmic periods; this increase lessening with convalescence. An addition of calcium phosphate and sodium chloride to iron salts increases their blood-forming action. W. D. H.

Phloridzin Diabetes. By FREDERICK W. PAVY (*Proc. Physiol. Soc.*, 1896, 19—22).—The statement has been made that in phloridzin diabetes there is no glycohæmia. The present communication shows that if fallacies in the collection of blood, in the use of anæsthetics, and in the method employed for analysis of the blood, be avoided, there is a distinct rise in the percentage of sugar in the blood as a result of giving the drug. W. D. H.

Action of Carbon Bisulphide on Hæmoglobin. By NICOLAI KROMER (*Virchow's Archiv*, 1896, **145**, 188—190).—Death produced by carbon bisulphide is due to paralysis of the respiratory centre, not to any change in the blood pigment, for although this reagent causes, after the lapse of time, a partial precipitation of proteid matter, the spectrum seen is that of oxyhæmoglobin. This occurs in experiments performed in the living body and *in vitro*; there is no formation of methæmoglobin or hæmatin, as some observers have described. W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Suitability of Nodule-Bacteria of Different Origin for Various Kinds of Leguminosæ. By FRIEDRICH NOBBE and LORENZ HILTNER (*Landw. Versuchs-Stat.*, 1896, **47**, 257—268).—Representatives of the six principal groups of the *Papilionaceæ* were grown in pots containing a mixture of sand and soil. One plant in each case was left without inoculation, the other five being inoculated with pure cultivations of nodule bacteria from (1) *Phaseolus multiflorus*, (2) *Pisum sativum*, (3) *Trifolium pratense*, (4) *Robinia pseudacacia*, (5) *Lupinus luteus*, and (6) *Ornithopus sativus* respectively. The plants selected for experiment were (1) *Phaseolus multiflorus*, (2) *Pisum sativum*, *Vicia villosa*, and *Lathyrus sylvestris*, (3) *Trifolium pratense* and *Medicago sativa*, (4) *Robinia pseudacacia*, (5) *Lupinus luteus* and *Anthyllis vulneraria*, (6) *Ornithopus sativus*. Each pot contained air-dried garden soil (1·2

kilos. containing 3·45 grams of nitrogen), pure quartz sand (6·8 kilos.), KCl (0·5 gram) and $Ca_3(PO_4)_2$ (5·0 grams). The following table shows the amount of water evaporated from the plants, indicating the relative amount of growth in each case, and also the total nitrogen in the produce.

	Inoculated with bacteria from					
	Phaseolus.	Pisum.	Trifolium.	Robinia.	Lupinus.	Not inoculated
Evaporation (litres).						
1. Phaseolus mult...	20·17	8·66	17·46	12·65	12·89	11·30
2. *a.* Pisum sativum	18·31	46·26	6·33	4·93	5·56	3·62
2. *b.* Vicia villosa..	35·46	44·48	—	6·91	5·76	3·96
2. *c.* Lathyrus sylv.	3·09	8·10	4·71	3·70	5·43	5·65
3. *a.* Trifol. prat. ...	9·01	6·25	35·83	7·82	6 58	—
4. Robinia pseudac.	3·57	4·53	5·85	14·82	4·23	5·46
Total Nitrogen (milligrams).						
1. Phaseolus mult...	878	—	—	—	—	160
2. *a.* Pisum sativum	853	2,791	125	105	142	56
2. *b.* Vicia villosa...	2,310	3,444	—	280	144	79
2. *c.* Lathyrus sylv.	49	384	68	62	78	81
3. *a.* Trifol. prat. ...	392	108	2,136	123	123	—
4. Robinia pseudac.	52	51	74	509	57	82

In the case of *Medicago sativa,* inoculation with Trifolium-bacteria had very little effect, whilst the other bacteria seemed to have no effect at all. The lupins failed. With regard to Anthyllis, the plants all grew much alike; only the Robinia bacteria had a slight effect. None of the serradella plants had nodules.

The results show that inoculation is only certain when bacteria from similar plants are used. Mutual availability, without essentially lessened effect, was observed only in the case of the *Viciaceæ.* Phaseolus-bacteria are effective for all the *Viciaceæ,* but the inoculation was much retarded. Pisum-bacteria were only available for the *Viciaceæ* and for *Phaseolus,* and Robinia-bacteria only for *Robinia.*

The most obvious effect of inoculation was increased vigour and development of the plants; increased flower and fruit production was also observed, especially in the case of peas and red clover. Generally, the vegetating period is prolonged by inoculation.

A period of hunger was never observed when bacteria corresponding with the plant were employed for inoculation, but when, for instance, peas and vetches were inoculated with Phaseolus-bacteria there was a long period of hunger. In sand cultures, there may be a period of hunger even when the plants are suitably inoculated, owing to the nodules not being fully developed by the time the supply of nitrogen of the seed is exhausted.

Root nodules have no essential influence on the above-ground growth as long as the soil contains sufficient nitrogen. As soon as soil nitrogen fails, leguminous plants which have no nodules are no longer able to develop. The leaves of *Leguminosæ* cannot, therefore, be the organs by means of which free nitrogen is assimilated.

N. H. J. M.

Action of the Oxidising Ferment of Mushrooms on various Oxidisable Compounds. By EMILE E. BOURQUELOT (*Compt. rend.*, 1896, **123**, 315—317).—The oxidising ferment of mushrooms acts on all the cresols. Orthocresol is oxidised in neutral, and also, though somewhat more slowly, in slightly alkaline solutions, with formation of a greenish-brown liquid and a dull green precipitate, soluble in ether; metacresol is oxidised under similar conditions, and yields a rose-white precipitate soluble in alcohol; paracresol is oxidised much more readily in a slightly alkaline than in a neutral solution, and the liquid becomes red and afterwards green, but the colouring matter is not soluble in ether.

Resorcinol is oxidised in neutral, but more readily in alkaline solutions, and the product is deep red with a green fluorescence.

Guaiacol is oxidised more readily in neutral or acid than in feebly alkaline solutions, and the change is very rapid; the liquid becoming orange-red, and soon depositing a red compound soluble in ether. Eugenol is oxidised under similar conditions, and a white precipitate of vanillin is formed, but no colouring matter.

Metatoluidine is oxidised very slowly in neutral solutions, but readily in presence of acetic acid, and yields a red-brown liquid and a violet precipitate; the products seem to be a wine-red substance, soluble in ether, and a violet substance insoluble in ether. Xylidine under similar conditions yields a violet-red product soluble in ether.

When aniline "for red" is dissolved in dilute acetic acid, mixed with a small quantity of an infusion of *Russula delica* and a current of air passed through the liquid, a substance of great tinctorial power, similar to magenta, is formed.

C. H. B.

Action of the Oxidising Ferment of Mushrooms on Insoluble Phenols. By EMILE E. BOURQUELOT (*Compt. rend.*, 1896, **123**, 423—425).—The oxidising effect of the ferment from mushrooms is exerted in solutions containing not more than 50 per cent. of ethylic or methylic alcohol, the oxidation of tyrosin, for example, taking place as readily in such solutions as in pure water. The methylic and ethylic alcohols are not affected by the ferment. These facts have been utilised to investigate the action of the ferment on various phenols insoluble in water.

Orthoxylenol yields a white precipitate, which afterwards becomes salmon colour; it is soluble in ether. Metaxylenol yields a white precipitate, which acquires a dull rose colour; it is largely soluble in ether. Paraxylenol yields a similar product which seems to be insoluble in ether.

Thymol in a slightly alkaline solution yields a white precipitate. Carvacrol in neutral solution yields a bulky white precipitate.

α-Naphthol solution becomes blue, and then violet, whilst a dull blue precipitate separates; it is partially soluble in ether, forming a mauve solution. β-Naphthol yields a white precipitate which gradually becomes yellow, and is almost completely soluble in ether. This difference might be used to distinguish between the two naphthols.

C. H. B.

Occurrence of Titanium. By CHARLES E. WAIT (*J. Amer. Chem. Soc.*, 1896, **18**, 402—404).—The author finds that titanium occurs in every plant ash which he has examined. Oak wood ash contains 0·31; apple and pear wood ash (mixed), 0·21; cow peas ash, 0·01; cotton-seed meal ash, 0·02 per cent. of titanium. The ash from bituminous and anthracite coal also contains titanium. The ash from Pennsylvanian anthracite coal contains as much as 2·59 per cent. J. J. S.

Composition of Wheat Germs. By S. FRANKFURT (*Landw. Versuchs-Stat.*, 1896, **47**, 449—470).—For qualitative examination, the germs were freed as far as possible from bran and portions of endosperm by repeated sifting, whilst the quantitative experiments were made with isolated germs picked out with the help of a lens.

In the aqueous extract employed in the examination for nitrogen compounds, albumoses, allantoin, asparagine, and a small amount of xanthine substances were found. Peptone was also present, but there is evidence that this does not exist in the germs, being produced during the digestion of the germs with warm water. Protein-dissolving ferments do not seem to be present in the free state, but in the form of a zymogen. Choline and betaine were detected, but attempts to isolate amido-acids failed. The ether extract yielded a relatively large amount of crude fat, containing lecithin and much cholesterol. With regard to carbohydrates, the germs contain cane sugar, raffinose, and small quantities of glucose, but no starch.

Wheat germs contain a ferment which vigorously inverts cane sugar at 40°, but has no effect on raffinose and very little on starch; this ferment, which is present in the free state in the germs, can be extracted by glycerol, and is precipitated by alcohol. As regards higher plants, such ferments seem only to have been hitherto detected in the pollen of *Corylus avellana* and *Pinus sylvestris* (A. von Planta, *Deut. Bienenzeitung*, 1879, No. 12).

The following quantitative results are given (per cent. in the dry substance).

Protein-Nitrogen.						
Insol. in hot water.	Soluble in hot water.	Amide nitrogen.	Crude fat.	Soluble carbohydrates.	Crude fibre.	Ash.
3·46	2·18	0·80	13·51	24·34	1·71	4·82

The crude fat includes lecithin (1·55 per cent.) and cholesterol (0·44 per cent.). The soluble carbohydrates include 6·89 per cent. of raffinose.

The results indicate that the germs contain abundant material to develop without the aid of the endosperm. The latter would, however,

protect and ensure the development of the germs under unfavourable conditions. N. H. J. M.

Constituents of the Seeds of Pharbitis Nil, L. By NICOLAI KROMER (*Arch. Pharm.*, 1896, **234**, 459—480).—The author summarises his results as follows. "(1) The fatty oil of the seeds consists of the glycerides of oleic, palmitic, and acetic acids, and of a stearic acid melting at 54°; in addition, it contains a small quantity of lecithin. (2) The seeds contain a tannin, $C_{17}H_{22}O_{10}$, which turns ferric chloride solution green, and yields a yellow lead derivative containing 50·33 per cent. of lead. (3) They contain besides a carbohydrate belonging to the saccharose group; this is dextrorotatory, $[\alpha]_D = +109·53°$. I propose the name *Pharbitose* for it. (4) The resinous glucoside of the seeds is insoluble in water, and contains no nitrogen; it is lævorotatory, and has the same percentage composition as convolvulin, but is not identical with that substance. Alkali hydroxides decompose it into a glucosidic acid isomeric with convolvulinic acid, a tetrahydroxydecylic acid, and fatty acids volatile with steam, probably methylethylacetic and tiglic acids. This glucosidic acid is insoluble in ether, and is hydrolysed by mineral acids to a carbohydrate (+glucose) and a fatty acid melting at 68·5°, in all probability isomeric with convolvulinolic acid." C. F. B.

Calculation of Proteids in Seeds from the Amount of Nitrogen. By C. HEINRICH L. RITTHAUSEN (*Landw. Versuchs-Stat.*, 1896, **47**, 391—400).—In 1872 it was pointed out that the ordinary method of calculating the proteids in grain, &c., by multiplying the percentage of nitrogen by 6·25, gives more or less incorrect results, inasmuch as the percentage of nitrogen in pure proteids is not 16 but 16·66 to 18·4. (Ritthausen "Die Eiweisskörper d.-Getreidearten.") In order to obtain a basis for the further discussion of the subject, the author has collected the most important results respecting the composition of the proteids of seeds, and these are given in tables. With regard to the cereals and pulses, the average percentage of nitrogen in the proteids is 17·6; whilst in the oil seeds it is 18·2. In these substances, therefore, the factors would be 5·7 and 5·5 respectively. Barley, maize, buckwheat, soja and white beans are, however, exceptions. In these the factor 6·0 should be employed (the proteids containing 16·66 per cent. of nitrogen). The same factor (6·0) holds also for rape and Brassica seeds, and candle-nut.

In the published results of analyses of foods the amount of nitrogen found is very frequently omitted, the percentage × 6·25 alone being given. The percentage of nitrogen has, therefore, to be calculated before the correct factor for proteids can be applied. In the case of substances in which the proteids have been insufficiently investigated or not at all, the factor 6·25 must, of course, be retained.

N. H. J. M.

Oxidation of Organic Matter in Soil. By PIERRE P. DEHÉRAIN and E. DEMOUSSY (*Compt. rend.*, 1896, **123**, 278—282).—When soil is heated to 120°, carbonic anhydride is produced, and the soil when

allowed to cool and re-inoculated undergoes more rapid nitrification than the original soil, seemingly in consequence of the partial oxidation of the organic matter.

The oxidation of the organic matter of sterilised soils by air at 22° is extremely small; non-sterilised soils are, however, slowly oxidised at this temperature with production of carbonic anhydride, which, however, is less than the volume of oxygen absorbed, some of the latter being used up in oxidising hydrogen or in forming an oxidation product which remains in the soil. The rate of oxidation is higher the more readily air can permeate the soil; it is also influenced by the proportion of water, and with rich soils oxidation at 22° or 44° is at its maximum when the soil contains 17 per cent. of water, but decreases if the proportion of water falls to 10 per cent. or rises to 25 per cent. With soils less rich in humus, a somewhat higher proportion of water is necessary to retard oxidation in any marked degree, although the same minimum proportion holds good. As oxidation continues, the rate of production of carbonic anhydride becomes less and less, a result no doubt due to the fact that humus is a complex substance, some of the constituents being more oxidisable than others.

When non-sterilised soil is heated, the rate of oxidation increases slightly between 22° and 44°, becomes much more energetic at 65°, but falls off considerably at 80°, owing most probably to the destruction of the microbes. Beyond 96°, however, there is again a marked increase in the rate of oxidation. At 110° or 120° the volume of carbonic anhydride liberated is greater than the volume of oxygen absorbed, and part of the former must result from decomposition and not from oxidation. At 100°, the carbonic anhydride produced is less than the volume of oxygen absorbed, just as at 22°, water or some other oxidation product being formed. Similarly, the rate of production of carbonic anhydride at 100° falls off as the oxidation progresses.

Oxidation is so active between 40° and 60° that it is conceivable that in hot climates soils left unworked and without manure may gradually become sterile owing to the disappearance of the humus. Even at Grignon, some fields carrying various crops without addition of manure have lost half their organic matter in 10 years.

C. H. B.

Destruction of Fat by Moulds. By C. Heinrich L. Ritthausen and Baumann (*Landw. Versuchs-Stat.*, 1896, **47**, 389—390).—The following analyses are given of two samples of rape cake, (1) in their original state, and (2) after they had been kept for two years in a finely powdered state in stoppered bottles. The samples became covered with mould.

	Sample I.			Sample II.		
	Water.	Fat.	Nitrogen.	Water.	Fat.	Nitrogen.
In original state	12·45	10·53	5·13	12·31	8·50	4·86
After two years (mouldy)	21·94	1·98	5·15	23·42	1·87	5·12

The excess of water in the mouldy samples can only have been derived from the decomposed fat. Fifteen different bacteria and fungi

were isolated, and it is assumed that it is mainly to the moulds that the changes observed were due. (Compare Reitmair, Abstr., 1891, 770). N. H. J. M.

Maize-germ Cake. By F. J. van Pesch (*Landw. Versuchs.-Stat,* 1896, **47**, 473—475).—Maize-germ cake is a product of oil factories and is obtained in a manner similar to linseed cake. It is used as food for all kinds of cattle. The following analyses of samples of cake, stated to be "maize cake" but which were undoubtedly maize-germ cake, are given.

	Water.	Crude protein.	Fat.	N-free extract.	Crude fibre.	Ash.
1.	18·8	16·2	3·6	56·7	2·7	2·0
2.	17·2	17·8	4·0	59·0		2·0
3.	10·8	17·5	4·2	61·4	3·7	2·4
4.	13·6	20·2	5·7	54·6	4·4	1·5
5.	12·1	22·7	5·3	53·9	4·3	1·7

Maize-germs contain, according to Moser; water 11·8, proteids 12·4, fat 17·4, nitrogen-free extract 46·0, crude fibre 6·9, and ash 5·5 per cent. N. H. J. M.

Analytical Chemistry.

A Convenient Form of Graduated Flask. By WILHELM WISLICENUS (*Ber.*, 1896, **29**, 2442—2445).—The author points out that Biltz's modified measuring flask (Abstr., 1896, ii, 671) is not new, he has himself for several years used a modification in which the neck of the flask is widened above the ordinary graduation mark and again constricted higher up, a second graduation mark being placed above the wider portion so that this contains exactly 100 c.c. between the two marks. In the preparation of a standard solution, 1100 c.c. are first prepared of slightly greater strength than is required. A portion of the liquid is then removed from the upper part of the flask, its strength accurately determined, and from this the amount of water to be added to 1000 c.c. is calculated. The flask is then emptied by means of a pipette down to the 1000 c.c. mark and the requisite amount of water added. A. H.

NOTE.—This arrangement is identical with that described by Giles (Abstr., 1894, i, 251).—EDS.

Iodometric Estimation of Selenious and Selenic Acids. By JAMES F. NORRIS and HENRY FAY (*Amer. Chem. J.*, 1896, **18**, 703—706).—Selenious acid may be estimated by mixing a measured portion of the solution containing it with ice-cold water and 10 c.c. of hydrochloric acid (sp. gr. 1·12), adding an excess of N/10 sodium thiosulphate solution, and titrating back with iodine solution. One mol. of selenious acid is equivalent to 4 mols. of sodium thiosulphate. The exact nature of the chemical change has not yet been ascertained. The

hydrochloric acid must be sufficient to liberate all the thiosulphuric acid. Before applying this method, the selenic acid is reduced by adding 25 c.c. of concentrated hydrochloric acid to a measured portion of the solution, diluting to 100 c.c. and boiling for one hour, care being taken that the volume is never less than 75 c.c. The cooled liquid is then treated as described above, except that it will probably be already sufficiently acid. A. G. B.

Separation of Selenium from Tellurium. By FRANK A. GOOCH and A. W. PEIRCE (*Amer. J. Sci.*, 1896 [4], 1, 181—185).—The fact that selenium bromide is volatile, whereas tellurium bromide is not, can be made use of in estimating selenium in the presence of tellurium. With the object of testing the accuracy of the method, the author has experimented in the following way. Solutions containing known weights of selenious and tellurous anhydrides, dissolved in potash, were treated with excess of phosphoric acid in order to dissolve the precipitate which was formed at first. One gram of potassium bromide was added, and the whole introduced into a Voit flask and water added to make the volume up to 50 c.c.; this first flask was fused to a second Voit flask containing 10 c.c. of water, and the second flask, in its turn, was fused to a Drexel bottle which had fused to its escape tube a Will and Varrentrap bulb to serve as a trap. The bottle and bulbs were filled with potassium iodide solution, and carbonic anhydride was kept slowly passing through the whole apparatus. The distillation of the products in the first flask was continued until the 50 c.c. had been reduced to 15 c.c.; by this time all the selenium had passed over in the form of its bromide and had been collected in the second flask, a small quantity of iodine had also been liberated in the bottle owing to bromine having passed over. As a quantity of selenium bromide collected in the tube connecting the two flasks, it was necessary to drive this over into the second flask before disconnecting. The first flask was then removed, 1 gram of potassium iodide was added to the second flask, the current of carbonic anhydride was again started through the apparatus, and the mixture was boiled for 10 mins. The free iodine in the flask, Drexel bottle and trap was taken as the measure of the selenious anhydride present. The results were fairly good, the errors being 0·1—0·7 per cent. J. J. S.

Estimation of Tellurium by Precipitation as the Iodide. By FRANK A. GOOCH and W. C. MORGAN (*Amer. J. Sci.* [4], **2**, 271—272, and *Zeits. anorg. Chem.*, 1896, **13**, 169—171).—Tellurous acid may be very accurately estimated by simply adding standard solution of potassium iodide as long as it forms a precipitate. The liquid should contain at least one-fourth of its bulk of strong sulphuric acid, and when the greater part of the tellurium iodide has formed the beaker must be rotated to make the precipitate settle. More potassium iodide is then added to complete the reaction. Ten test experiments are given to show the accuracy of the process. L. DE K.

Nitrates in Water. By ALESSANDRI and GUASSINI (*Chem. Centr.* 1896, i, 329; from *Boll. Chim. farm.* 1895, 490).—A few c.c. of the

sample is evaporated to dryness, and 6 drops of a saturated solution of phenol in hydrochloric acid is at once added. Sometimes it is advisable to slightly warm the reagent. If nitrates are present, a reddish-violet coloration is obtained which on adding ammonia changes to an emerald green. L. DE K.

Iodometric Method for the Estimation of Phosphorus in Iron. By CHARLOTTE FAIRBANKS (*Amer. J. Sci.* [4], **2**, 181—185, and *Zeits. anorg. Chem.*, 1896, **13**, 117—120).—The method for titrating molybdic acid with iodine recommended by Gooch and Fairbanks (this vol., ii, 76) is also applicable to the yellow molybdic precipitate, and is, therefore, a convenient process for the estimation of phosphorus in iron. Twelve mols. of molybdic acid correspond with 1 atom of phosphorus. L. DE K.

Estimation of Phosphates in Precipitates. By THEODOR PFEIFFER (*Landw. Versuchs-Stat*, 1896, **47**, 357—360).—Determinations of phosphoric acid in a sample of precipitate gave the following results. With strong hydrochloric acid as solvent, $P_2O_5 = 30{\cdot}96$ and 31·10 per cent.; with aqua regia $P_2O_5 = 33{\cdot}00$ and 32·91 per cent.; with a mixture of sulphuric and nitric acids $P_2O_5 = 33{\cdot}19$ per cent. It was found that the whole of the phosphoric acid in hydrochloric acid extracts is not precipitated by magnesia mixture (citrate method), and that the filtrate yielded a further amount (2·27 per cent.), when boiled with sulphuric or nitric acid. This seems to be due to the presence of pyrophosphate in the precipitate. When pure monocalcium phosphate (5 grams) was heated for a long time at 250°, dissolved in boiling hydrochloric acid, and diluted to 250 c.c., 62·64 per cent. of P_2O_5 was found by direct precipitation, and 68·99 per cent. after boilimg with nitric acid.

Two samples of precipitate (one of which had been slightly dried and the other not at all) were found to be free from pyrophosphate. Another sample which had been dried by heating with steam showed a distinct amount of pyrophosphate; whilst a fourth sample from England, which had been over-dried, gave a percentage of 31·10 of P_2O_5 before, and 32·91 after the "inversion" of the hydrochloric acid solution.

The results show that mere estimation of total phosphoric acid is misleading, especially when aqua regia is employed as the solvent. N. H. J. M.

The Precipitation of Phosphomolybdate in Steel Analysis. By GEORGE AUCHY. (*J. Amer. Chem. Soc.*, 1896, **18**, 170—174).—In order to ensure the complete precipitation of the phosphorus, the following process is recommended:—Two grams of steel is dissolved in 100 c.c. of nitric acid of sp. gr. 1·13, the solution is partially neutralised by adding 15 c.c. of strong ammonia previously diluted with 50 c.c. of water, and after heating to 85°, the phosphoric acid is precipitated by adding 60 c.c. of Blair and Whitfield's molybdate solution.

If it is thought desirable to precipitate from a very acid solution,

from 15—20 grams of ammonium nitrate should be first added and the liquid should be somewhat diluted. The author adds a caution as to the occasional presence of phosphoric acid in the reagents used.

L. DE K.

Interaction of Chromic and Arsenious Anhydrides. By PHILIP E. BROWNING (*Amer. J. Sci.*, 1896 [4], 1, 35—37).—Kessler has shown (*Pogg. Annalen*, 1855, **95**, 204) that arsenious anhydride may be estimated by treating it in the presence of hydrochloric acid with an excess of a chromate of known strength. The excess of chromic acid is then determined by the addition of a ferrous salt until a drop taken from the solution gives a blue colour with a ferricyanide. Chromic acid is again added until the blue colour disappears.

The author shows that a somewhat similar method may be used for estimating chromic acid. The chromate solution is mixed with about 10 c.c. of dilute hydrochloric or sulphuric acid (1 : 4) and a carefully measured amount of N/10 arsenious acid solution is run in; care must be taken that the arsenious acid is in excess. It is not necessary to apply heat to bring about the reduction of the chromate. About 5 grams of potassium or sodium hydrogen carbonate are added to the solution, and in most cases a precipitate forms unless Rochelle salt has been previously added, N/10 iodine is then run in until the solution acquires a slightly permanent yellow colour, and the mixture is allowed to stand for about 30 minutes. The excess of iodine is destroyed by N/10 arsenious acid, starch is added, and the solution titrated with N/10 iodine.

The points to notice are that the addition of Rochelle salt gives a dark green solution and thus renders it difficult to detect the point where the iodine gives the blue colour with starch. If Rochelle salt is not added, a precipitate forms, and this contains small quantities of arsenious acid unless it is allowed to remain for some time (1—2 hours) with the excess of iodine. The method is fairly accurate, and can be carried out in the presence of ferric salts.

J. J. S.

Detection and Estimation of Borax in Butter. By VICTOR PLANCHON and VUAFLART (*J. Pharm.*, 1896 [6], **4**, 49—51).—The amount of borax present in a sample of butter can be roughly estimated by means of a colour reaction, depending on the formation of a blue compound produced by the fusion of copper oxide with borax. The ash from 20 grams of butter is fused with 0·5 grams of potassium carbonate, and a trace of copper oxide. The amount of borax present may be estimated approximately from the intensity of the blue colour produced.

M. W. T.

Estimation of Silicon in Pig Iron. By LIEBRICH (*Chem. Centr.*, 1896, i, 68—69; *Stahl u. Eisen*, **15**, 1058).—The filter containing the silicic acid, silicon, and graphite is, without removing the iron, burnt, and the black ash is fused with dehydrated potassium hydrogen sulphate until all the carbon has disappeared. The residue, on being digested with hydrochloric acid, leaves pure silicic acid free from titanium and iron.

L. DE K.

Detection and Estimation of Carbonic Oxide in Air. By JOHN S. HALDANE (*J. Physiol.*, 1896, **20**, 521—522).—The method previously described for estimating the percentage of carbonic oxide in the air by means of a solution of blood requires modification in view of the fact that daylight has a marked influence on the stability of carboxy-hæmoglobin. The precautions to avoid the influence of strong light, and the necessary alterations in the table are given.

W. D. H.

Separation and Identification of Potassium and Sodium. By D. ALBERT KREIDER and J. E. BRECKENRIDGE (*Amer. J. Sci.*, [4], **2**, 263—268, and *Zeits. anorg. Chem.*, 1896, **13**, 161—168. Compare Abstr., 1895, ii, 444).—Potassium may be completely separated from sodium by evaporating the solution with perchloric acid and treating the residue with 97 per cent. (commercial absolute) alcohol, which soon dissolves the sodium compound, but leaves the potassium perchlorate which is quite insoluble. When dealing with a sulphate, this must first be decomposed by means of barium chloride, the excess of the latter being removed by ammonium carbonate, and the ammonium compounds expelled by ignition. The sodium is precipitated from its alcoholic solution as chloride by means of a current of hydrogen chloride, and may then be further identified. The perchloric acid must, of course, be quite free from sodium, and is, therefore, best purified by distillation under low pressure. Details for the safe preparation of the reagent are given.

L. DE K.

Volumetric Estimation of Alkali Hydroxides containing Carbonates and of Alkali Carbonates: The Value of Phenolphthaleïn and Methyl-orange as Indicators. By FRIEDRICH W. KÜSTER (*Zeits. anorg. Chem.*, 1896, **13**, 127—150).—The only method for the volumetric estimation of mixed solutions of alkali hydroxides and alkali carbonates which gives trustworthy results is that published by Cl. Winkler. The alkali carbonates are precipitated by barium chloride, and the solution, together with the precipitate, is titrated, using phenolphthaleïn as indicator. The total alkali is determined by titration, using methyl-orange as indicator. Methyl-orange is, contrary to the statements of previous authors, strongly coloured by carbonic acid; and in the titration of alkali containing carbonates the titration must be continued only to a known normal coloration which is defined by comparison with an equally concentrated aqueous solution of the methyl-orange saturated with carbonic anhydride. Phenolphthaleïn is also coloured by aqueous solutions of alkali hydrogen carbonates when these solutions are dilute. The coloration is weakened by the presence of sodium salts of strong acids and by carbonic anhydride, and disappears entirely in the presence of large quantities of free carbonic anhydride. This indicator cannot, therefore, be used for the direct volumetric estimation of alkali hydroxides contained in alkali carbonates. Trustworthy results are obtained only when a small quantity of carbonate is present, whereas by Winkler's method the results can be depended on irrespective of the amount of carbonate. In the presence of hydrogen alkali carbonates, the total alkali is determined with methyl-orange as indicator; the hydrogen carbonate

is estimated by adding a measured quantity of alkali hydroxide in excess, precipitating with barium chloride, and titrating, using phenolphthaleïn as indicator. The difference between the amount of alkali added and that found after precipitation gives the quantity of hydrogen carbonate present. The results obtained are too low, and the error is proportional to the amount of hydrogen carbonate present. E. C. R.

Estimation of Cadmium as Oxide. By PHILIP E. BROWNING and LOUIS C. JONES (*Amer. J. Sci.* [4], **2**, 269—270, and *Zeit. anorg. Chem.*, 1896, **13**, 110—112).—Muspratt has stated that the estimation of cadmium as oxide by igniting the carbonate gives results which are much below the truth; no better results are obtained by dissolving the carbonate in nitric acid and igniting the nitrate. The authors state that when using the Gooch asbestos filter and crucible, the carbonate may be converted into oxide without loss. Twenty-one experiments are quoted to show the trustworthiness of the process.

L. DE K.

Estimation of Lead in Potable Waters. By UBALDO ANTONY and T. BENELLI (*Gazzetta*, 1896, **26**, ii, 194—195).—Potable waters may contain various substances, such as silicic acid, ferric, and aluminium hydroxides, in the colloidal state and, on adding the amount of ammonium chloride necessary for the complete precipitation of the lead and mercuric sulphides in accordance with the authors' method (Abstr., 1896, ii, 549) of estimating lead in water, these hydroxides would assume the insoluble form. It is recommended that after the lead sulphate has been weighed, it should be dissolved in hot ammonium tartrate solution, and any insoluble residue weighed and allowed for.

W. J. P.

Electrolytic Estimation of Mercury. By EDGAR F. SMITH and DANIEL L. WALLACE (*J. Amer. Chem. Soc.*, 1896, **18**, 169—170).—The amount of mercury in cinnabar may be conveniently estimated by dissolving about 0·22 gram of the mineral in 25 c.c. of solution of sodium sulphide (sp. gr. 1·2). After diluting to 125 c.c., the liquid is electrolysed in a platinum crucible at a temperature of 70° with a current of N.D. 100 = 0·12 ampère. The precipitation of the metal is complete within 3 hours. L. DE K.

New Method of Separating the Phosphates in the Ammonia Group. By N. TARUGI (*Gazzetta*, 1896, **26**, ii, 256—258).—The methods in general use for separating the precipitate of metallic phosphates obtained with ammonia and ammonium chloride in qualitative analysis being inconvenient, the author has devised the following process, which gives excellent results.

The precipitate is treated with cold acetic acid, when only ferric and aluminium phosphates and many of the oxalates remain undissolved; after filtration, all the phosphoric acid and part of the oxalic acid is removed from the filtrate by adding excess of lead acetate. The lead salt is filtered off and the filtrate freed from lead by adding hydrochloric acid and then hydrogen sulphide or thioacetic acid; after boiling off the hydrogen sulphide and filtering, the filtrate is poured

drop by drop into a boiling concentrated sodium carbonate solution into which the precipitate not dissolved during the first treatment with acetic acid has been put. The only phosphate the precipitate can contain is ferric phosphate, which, however, gives no trouble in the subsequent examination of the liquid for the metals.

If the original precipitate contains no oxalates, the part insoluble in acetic acid can only contain ferric and aluminium phosphates and need only be examined for these two metals; the acetic acid solution is then treated with ammonia and ammonium chloride and examined in the ordinary way. W. J. P.

Iodometric Estimation of Molybdic Acid. By FRANK A. GOOCH AND CHARLOTTE FAIRBANKS (*Amer. J. Sci.*, 1896 [4], 2, 156—162).—Mauro and Danesi recommend heating the molybdate compound with hydrochloric acid and potassium iodide in a sealed tube filled with carbonic anhydride. The liberated iodine is afterwards titrated. Friedheim and Euler prefer submitting the mixture to distillation and titrating the iodine in the distillate.

The authors have found that the molybdic acid is best estimated by acting on the residue with iodine in the presence of an alkali. A quantity of molybdic acid, in the form of an alkali salt, not exceeding 0·3 gram is mixed up with 20 c.c. of water, 20 c.c. of hydrochloric acid (sp. gr. 1·20) and 0·5 gram of potassium iodide, and after introducing the liquid into a narrow flask it is rapidly boiled down to 25 c.c. but not further. The residue, after adding 1 gram of tartaric acid, is nearly neutralised with aqueous soda, and then mixed with a slight excess of sodium hydrogen carbonate. A definite quantity of iodine solution is now at once added, and the corked bottle is set aside for 2 hours. The excess of iodine is titrated by means of arsenious oxide. One atom of iodine corresponds with 1 mol. of molybdic acid. L. DE K.

Application of the Blue Oxide of Molybdenum in Volumetric Analysis. By ATTILIO PURGOTTI (*Gazzetta*, 1896, ii, 197—220).—The blue oxide of molybdenum, Mo_3O_8, is readily oxidised by such substances as permanganates, chromates, hypochlorites, chlorine, peroxides, ferric salts, and platinic and auric chlorides, and since the oxidation of the whole of the oxide is rendered evident by the disappearance of the characteristic blue colour, it may be used for the volumetric estimation of oxidising agents. The reduction of molybdic anhydride occurs in two stages in accordance with the equations $5MoO_3 + 16H = Mo_5O_7 + 8H_2O$ and $Mo_5O_7 + 19MoO_3 = 8Mo_3O_8$, so that if a solution containing $5MoO_3$ be completely reduced to the brown oxide, Mo_5O_7, and then added to a solution containing $19MoO_3$, this will contain only the blue oxide. The standard solution of the blue oxide is made by reducing 1·1 gram of ammonium molybdate, $(NH_4)_6Mo_7O_{24}, 4H_2O$, dissolved in 30 c.c. of water and 5 c.c. of pure sulphuric acid with 4—5 grams of zinc dust; after filtering the brown solution, it is made up to 200 c.c. and added to a solution of 4·2 grams of ammonium molybdate and 2 c.c. of pure sulphuric acid in 800 c.c. of water. The solution is then boiled until blue, and on cooling is ready for use; it is approximately N/50, and cannot be made N/10 because of the

sparing solubility of the oxide. The standardising is performed by diluting 10 c.c. of N/100 potassium dichromate to 30 c.c., adding 3 c.c. of 1 : 3 pure sulphuric acid, and running the molybdenum solution into the hot solution until a persistent blue colour is observed; the solution does not change in strength if preserved in well-closed full vessels.

For the indirect estimation of substances such as cupric salts which are not reduced by blue molybdenum oxide, the author does not use standard ferrous sulphate solution but prefers to reduce them with alkaline chromium hydroxide solution and subsequently estimates the chromate formed by titration with molybdenum solution. 10 c.c, of 16 per cent. chrome alum solution is mixed with 30 c.c. of 30 per cent. caustic potash giving an alkaline solution of about 0·32 gram of chromium hydroxide; this is boiled for about 15 minutes with 10 c.c. of a cupric salt containing about 0·15 gram of copper. The excess of chromium hydroxide is thus rendered insoluble, and potassium chromate remains in solution; the latter is then estimated by filtering the solution, making up to a standard volume and titrating an aliquot part with molybdenum solution after acidification with sulphuric acid.

The titration of hot permanganate or hot dilute ferric solutions with molybdenum solution gives excellent results. Good results are obtained in the estimation of lead by precipitating it as chromate and filtering, washing and dissolving the precipitate in caustic potash; the solution is then acidified with sulphuric acid and titrated with molybdenum solution. Lead solutions may also be boiled with calcium hypochlorite in feebly acid solutions and the precipitated lead peroxide filtered, washed and boiled with the alkaline chromium hydroxide as described above. After separating the insoluble chromium hydroxide, the filtrate is acidified with sulphuric acid and titrated with molybdenum solution.

Silver chloride or sulphate may be estimated by boiling with alkaline chromium hydroxide, when metallic silver is formed; the chromate produced is then estimated with molybdenum solution. The results obtained with silver nitrate solution are rather too high owing to the slight action of the nitric acid on the molybdenum solution. Both mercuric and mercurous salts are reduced to metallic mercury by alkaline chromium hydroxide solution, and may be estimated indirectly by titrating the chromate with molybdenum solution. Nickel and cobalt salts are converted into the sesquioxides by heating with calcium hypochlorite or sodium hypobromite solution and may then be estimated in the same way as lead peroxide. Good test results were obtained with all the methods described above; the presence of nitric acid is, however, to be avoided in titration with molybdenum solution.

W. J. P.

Reactions of Tungsten. By E. Defacqz (*Compt. rend.*, 1896, **123**, 308—310).—When a tungsten compound is converted into tungstic acid, heated with four or five times its weight of potassium hydrogen sulphate and a few drops of sulphuric acid, and then mixed with sufficient concentrated sulphuric acid to prevent solidification on cooling, the liquid obtained gives colour-reactions with a large number

of organic compounds. The best results are obtained with phenols and alkaloids, and the most important of these reactions are as follows :—*phenol*, very intense deep red; *quinol*, very intense amethyst-violet; *catechol*, violet black; α- or *β-naphthol*, violet-blue; *salicylic acid*, very intense deep red; *veratrine*, intense sienna colour. Many of the alkaloids give no coloration, and of the various compounds used phenol and quinol are the most valuable for analytical purposes, the reaction with them being much more sensitive than the well-known production of a blue coloration by the action of zinc or some similar metal. As a rule, the colorations disappear on adding water. C. H. B.

Reduction of Vanadic Acid by Hydriodic and Hydrobromic Acids, and its Titration in Alkaline Solution with Iodine By PHILIP E. BROWNING (*Amer. J. Sci.*, [4], **2**, 185—188, and *Zeits. anorg. Chem.*, 1896, **13**, 113—116).—The solution containing the vanadate is boiled in an Erlenmeyer beaker with potassium iodide or bromide and a regulated amount of sulphuric acid, until no more iodine or bromine is liberated. After cooling, the residual liquid is nearly neutralised with aqueous potash, a small quantity of tartaric acid is added, and the neutralisation completed with an excess of potassium hydrogen carbonate. Excess of standard iodine is then added, and after remaining for half an hour in a closed bottle, the free iodine left is estimated by means of a solution of arsenious oxide.

One mol. of iodine represents 1 mol. of vanadic acid. L. DE K.

Estimation of Bismuth. By WILHELM MUTHMANN AND F. MAWROW (*Zeits. anorg. Chem.*, 1896, **13**, 209—210).—The faintly acid solution of the bismuth salt is treated with an excess of hypophosphorous acid, and warmed on the water bath until the supernatant liquid is clear and a further addition of hot hypophosphorous acid does not cause any coloration. The reddish-grey precipitate of metal thus obtained is easily collected; after being washed with hot water, and with absolute alcohol, it is dried at 105°, and weighed either on a tared filtered paper or in a Gooch's crucible. The results are very accurate. The method is especially useful for the separation of bismuth from those metals which are not precipitated by hypophosphorous acid, such as zinc and cadmium.

E. C. R.

Platinum Amalgam and its Application in Analysis. By N. TARUGI (*Gazzetta*, 1896, **26**, i, 425—431).—Magnesium precipitates the whole of the mercury and platinum, from a solution containing both mercuric and platinic chlorides, as a black precipitate in which, even when it contains only 1 per cent. of platinum, no metallic mercury can be detected under the microscope. Further, the precipitate is always readily soluble in concentrated nitric acid, even if it only contains 1 per cent. of mercury, but if precipitated mercury and platinum be mixed, nitric acid dissolves mercury alone from the mixture; the solubility of the amalgam is therefore not due to the retention of chlorine by the precipitated metals.

The author proposes to apply these facts to the qualitative analysis of solutions which may contain gold, mercury, and platinum. The gold is first precipitated by oxalic acid, and, after separating it, magnesium is added to the filtrate; a grey precipitate can only be mercury, a black precipitate insoluble in nitric acid is platinum, whilst a black precipitate soluble in nitric acid shows that both platinum and mercury are present. W. J. P.

Separation of Palladium from Platinum. By PAUL COHN and FRANZ FLEISSNER (*Monatsh.*, 1896, **17**, 361—364).—The solution of the two metals in aqua regia is repeatedly evaporated with water in order to eliminate nitric acid, and again with about 10 c.c. of a 10 per cent. solution of ammonium chloride. The residue is then warmed with a few drops of water, and covered with a 30 per cent. solution of ammonium chloride, when ammonium platinochloride is gradually precipitated, this is separated by filtration, and washed, first with a solution of ammonium chloride and then with alcohol, and is finally transferred to a platinum crucible and heated to redness. The palladium chloride present in the filtrate is mixed with fairly strong nitric acid, and the whole evaporated on the water bath, when a beautifully crystalline red precipitate is formed; this is collected, and washed with a strong solution of ammonium chloride to which a few drops of nitric acid have been added. The precipitate consists of *ammonium palladiochloride*, $Pd(NH_4)_2Cl_6$; if insufficient nitric acid has been used, a brown basic salt is obtained instead.

The red ammonium palladiochloride is sparingly soluble in cold water, and is decomposed by warm water, with production of ammonium palladious chloride, $(NH_4)_2PdCl_4$; even in the cold solution, a slow decomposition takes place. It may be used for the estimation of palladium, being decomposed when heated in an atmosphere of coal-gas, leaving a residue of palladium. A series of experiments have served to show that, by observing the above conditions, the amounts of platinum and palladium in a mixture of their chlorides may be accurately estimated. A. L.

Technical Analysis of Asphaltum. By LAURA A. LINTON (*J. Amer. Chem. Soc.*. 1896, **18**, 275—279).—The author gives a few more instructions as to the assay of asphaltum (Abstr., 1895, ii, 333). In estimating the moisture, the temperature should not exceed 50°, and the drying is best effected by heating the sample in a current of dry air; the dried sample is then tested as directed.

It is now recommended to fraction the asphaltene by estimating the portion soluble in boiling turpentine and that soluble in chloroform only. After removing the petrolene, the residue on the filter is digested in boiling turpentine until the filtrate is colourless; the filter is then washed with alcohol and dried at 100°. If a black semi-liquid substance separates from the mass, the extraction with turpentine should be repeated; the residue on the filter is finally exhausted with chloroform to remove the portion undissolved by the turpentine. "Aged" varieties of asphaltum contain a larger proportion of asphal-

tene, but the fraction soluble in turpentine is smaller, whilst that soluble in chloroform is larger. L. DE K.

Estimation of Glucose in Urine. By B. A. VAN KETEL (*Zeit. physiol. Chem.*, 1896, **22**, 278—280).—The method originally used in the estimation of sugar in milk may also be used for the estimation of sugar in urine which is also rich in uric acid, or contains proteid or blood. To 50 c.c. of the liquid, 4 c.c. of liquid phenol and 10 c.c. of a 10 per cent. aqueous solution of lead acetate are added, and the mixture shaken and filtered. The filtrate, to which are added the washings of the filter, the whole being brought up to 100 c.c., can then be examined for sugar by the polarimeter, or after removal of the lead, and dilution, by means of Fehling's solution. Osazone crystals can also be prepared. W. D. H.

Estimation of Sugar in Blood. By FREDERICK W. PAVY (*Proc. Physiol. Soc.*, 1896, 7—10.)—The importance of the estimation of sugar in blood correctly is obvious. The difficulties of the analysis are great, because the proteids present must first be got rid of by precipitation in a form that lends itself to thorough washing. The author's alcohol method still holds; but the last traces of proteid in the alcoholic extract are best got rid of by boiling with hydrated alumina. W. D. H.

Polarimetric Estimation of Milk Sugar in Human Milk. By PAUL THIBAULT (*J. Pharm.*, 1896 [6], **4**, 5—10.)—In the analysis of cows' milk, acetates of lead or mercury, or sodium metaphosphate may be used to precipitate the proteids and fat. In dealing with human milk, however, these reagents do not give a liquid clear enough for optical examination. The author finds that a solution, containing, in 1 litre, 10 grams of picric acid and 25 c.c. of glacial acetic acid, when added to an equal volume of human milk gives, after filtration, a perfectly clear liquid, in which the milk sugar can be easily estimated by the optical method. A method is also given for the determination of the volume occupied by the fats, &c., previously separated. (Compare Wiley and Ewell, Abstr., 1896, ii, 628.) M. W. T.

Gravimetric Estimation of Sugars, especially of Maltose, by means of Fehling's Solution. By HARTOG ELION (*Rec. Trav. Chim.*, 1896, **15**, 116—122).—In the estimation of sugars by Fehling's solution, it is always advisable to oxidise the cuprous oxide to cupric before reducing it in a current of hydrogen. (Compare Abstr., 1891, 368.)

Another error in the estimation is caused by the action of the alkali on the asbestos filter; this error may be eliminated to a large extent by taking the mean weight of the filter before and after the experiment.

A third error, due to a secondary decomposition of the Fehling solution, may be eliminated by making a blank experiment, using an equal quantity of water instead of the sugar solution.

The author finds that in the case of maltose the Fehling's solution is reduced at the end of 2 mins., so that longer boiling is unnecessary.

J. J. S.

Rapid Process for the Detection of Formaldehyde in Milk. By Georges Denigès (*J. Pharm.*, 1896, [6], **4**, 193—195).—Ten c.c. of milk is diluted with water and, after the addition of two or three drops of acetic acid and some potassio-mercuric iodide, the solution is filtered. One c.c. of Schiff's reagent (magenta decolorised by sulphurous acid) is then added, and, after 10 mins., 2 c.c. of hydrochloric acid. The amount of formaldehyde present is indicated by the depth of the violet colour produced.

M. W. T.

Estimation of Hydrocyanic Acid in Officinal Waters. By Carl Glücksmann (*Chem. Centr.*, 1896, i, 329; from *Pharm. Post.*, **28**, 569—570).—The author has not succeeded in getting trustworthy results by Mohr's copper sulphate process, the end reaction being very uncertain. Other investigators also condemn the method.

L. de K.

Palmarosa Oil. By Eduard Gildemeister and Karl Stephan (*Arch. Pharm.*, 1896, **234**, 321—330).—See this vol., i, 81.

Estimation of the Constituents of a Mixture of Primary, Secondary and Tertiary Amines of the same Radicle. By Charles Gassmann (*Compt. rend.*, 1896, **123**, 313—315).—The method described was worked out with special reference to the ethylenediamines. The dried mixture is dissolved in a definite quantity of water, and an aliquot part is titrated with normal hydrochloric acid, using phenolphthaleïn as indicator. An equal volume is then mixed with one and a half times the volume of normal hydrochloric acid indicated by the first experiment, diluted with twice its volume of alcohol, cooled with ice, and titrated with normal sodium nitrite solution, using starch paste and potassium iodide as indicator.

If Mx, My, and Mz are the respective molecular weights of the mono-, di- and tri-amines, A the weight of the mixture taken, B the number of c.c. of normal acid, and C the number of c.c. of normal nitrite solution required by A, then x, y, and z, the respective quantities of the mono-, di-, and tri-amines present in A are given by the equations.

$$x = \frac{[(My - Mz)C + (BMz - 1000A)]Mx}{1000(My - Mx)}.$$

$$y = \frac{[1000A - BMz + C(Mz - Mx)]My}{1000(My - Mx)}$$

$$z = \frac{(B - C)Mz.}{1000}$$

For the ethylenediamines Mx = 59·56, My = 85·90 and Mz = 111·84 and the equations become

$$x = 0{\cdot}12706B - (2{\cdot}27216A + 0{\cdot}02947C)$$
$$y = 3{\cdot}3114A - 0{\cdot}18517B + 0{\cdot}0859C$$
$$z = 0{\cdot}05592(B - C).$$

The results are accurate to 0·33 to 0·5 per cent. C. H. B.

Qualitative Examination of Acetanilide. By CHARLES PLATT (*J. Amer. Chem. Soc.*, 1896, **18**, 142—146).—The following tests are recommended : strong cold nitric acid gives a colourless solution which on gentle heating turns first yellow and then brownish-red, evolving oxides of nitrogen. The cold solution also gradually assumes a brown colour, and deposits red, acicular crystals having an odour of nitrobenzene. If the nitric acid solution is rapidly evaporated to dryness, an oily residue of decided odour is left, but on slow evaporation a crystalline residue of slight odour is obtained. Dilute nitric acid dissolves the acetanilide in the cold with separation of oily globules ; and this solution, on slow evaporation, gives a brown residue with slight purplish tint. When boiled with the dilute acid, a colourless solution is obtained, and pungent fumes are evolved.

Strong sulphuric acid dissolves the compound yielding a colourless liquid which is not affected by boiling. The cold solution gradually acquires a pink or even brown colour, gradually changing to orange when viewed by reflected light ; subsequently, tufts of delicate acicular crystals appear, and the liquid becomes colourless.

Sulphuric acid and potassium dichromate give a dark green solution. If the solution of the compound in strong sulphuric acid is diluted before adding the chromate, no reaction is at first obtained, but gradually a reddish-brown colour is developed, changing to a dark olive-green.

Hydrochloric acid, alone or in conjunction with potassium dichromate, gives no marked reaction, but if the compound is dissolved in hydrochloric acid and then mixed with a weak solution of chromic acid a dark green coloration is finally observed. Aqueous potash produces a blue precipitate in this solution.

Bromine water added to the hydrochloric acid solution yields a heavy yellowish precipitate of bromaniline ; chlorine water, or a solution of bleaching powder, yields, however, no precipitate but gives a dark blue coloration which soon fades. If, before adding the bleaching powder, a few c.c. of a saturated solution of phenol is added, a brownish red colour is produced which turns blue on adding ammonia.

Aqueous potash liberates aniline, and if chloroform is also added, the mixture on heating gives the characteristic isonitrile reaction.

Sulphuric acid and sodium nitrite produce a fine red colouration.

Ferric chloride gives no reaction. Zinc chloride at a temperature of 270° causes the formation of a small quantity of flavaniline, a yellow substance with a green fluorescence. After acetanilide has been boiled with dilute nitric acid and potassium nitrite, the liquid turns deep red on boiling it with Plugge's reagent (a solution of mercurous nitrate containing nitrous acid). By means of these tests, acetanilide may be distinguished from antipyrine and phenacetine. Antypyrine also differs from acetanilide in being precipitated by mercuric chloride.

L. DE K.

Estimation of Caffeine. By MOSES GOMBERG (*J. Amer. Chem. Soc.*, 1896, **18**, 331—342).—See this vol., i, 129.

Estimation of Caffeine. By GEORGES (*J. Pharm.*, 1896 [6], **4**, 58—59).—0·5 gram of the finely powdered sample is mixed with fine sand, and thoroughly extracted with a 1 per cent. solution of sodium salicylate. The liquid is evaporated to about 50 c.c., and then shaken with chloroform; on evaporating the chloroform, the caffeine is left in a state of purity.

M. W. T.

Estimation of Caffeine in Tea. By MARIUS L. Q. VAN LEDDEN HULSEBOSCH (*Chem. Centr.*, 1896, i, 332; from *Pharm. Centr.*, **36**, 742).—Five grams of dry powdered tea is mixed with 1 gram of calcium hydroxide and heated with 100 c.c. of water on the water bath for 3 hours. After restoring the loss caused by the evaporation, the liquid is filtered and 50 c.c. of it is mixed with 0·5 gram of sodium carbonate. After filtering and evaporating the liquid to about 15 c.c., it is introduced into an extractor and submitted to the action of ether for 3 hours; the ethereal solution on evaporation leaves pure caffeine. The author thinks the process may be applied to coffee, cocoa and kola.

L. DE K.

Testing Quinine. By MELCHOIR KUBLI (*Chem. Centr.*, 1896, i, 224—225; from *Pharm. Zeit. Russ.*, **34**).—The author (compare Abstr., 1896, ii, 550) proposes another test for the purity of quinine sulphate, based on the following interesting reaction. When a neutral solution of quinine sulphate is precipitated by means of sodium carbonate, the liquid becomes clear again on adding solution of sodium hydrogen carbonate; but on passing a current of carbonic anhydride, the quinine is precipitated as normal carbonate, the volume of which may be measured in a graduated tube.

The presence of the salts of other cinchona alkaloids (hydroquinine excepted) exercises a remarkable influence on the volume of the precipitate, also on its appearance. Several examples are given.

L. DE K.

Estimation of Quinine Salts by Means of Sodium Nitroprusside. By I. G. KRAMERS (*Rec. Trav. Chim.*, 1896, **15**, 138—147).—On the addition of a solution of sodium nitroprusside to a solution of a neutral salt of quinine, small tarry drops separate, which collect on the sides and bottom of the vessel, and then gradually change to salmon-coloured needles. A dilute solution of quinine (1 in 100), when heated to 80° and then treated with the nitroprusside, yields no permanent precipitate at first, but on keeping at the same temperature for some time the salmon-coloured needles separate, and on cooling more crystals are formed, but no tarry matter. These needles have the composition $(C_{20}H_{24}N_2O_2)_4, Fe_2(CN)_{10}(NO)_2H_4 + H_2O$. They are insoluble in ether and benzene, sparingly soluble in cold alcohol, more readily in hot. They melt and decompose at 177—185°, and at the same time become blue. The moist crystals also turn blue when exposed to bright sunlight or when heated above 105°, and they are only slightly hygroscopic.

The only other alkaloid which gives a similar sparingly soluble compound with sodium nitroprusside is hydroquinine.

1·07 milligram of cinchonidine, 1·62 of quinidine, 2·68 of cinchonine, and 5·74 of homocinchonidine in 1 c.c. solution yield no crystalline precipitates. The method can therefore be made use of for testing the purity of quinine salts. The quinine is precipitated by means of the nitroprusside, and a few drops of ammonia are added to the filtrate, when, if the salt is pure, no precipitate will be formed. J. J. S.

Estimation of the Alkaloids in Nux Vomica. By C. C. Keller (*Chem. Centr.*, 1896, i, 228; from *Schweitz. Woch. Chem. Pharm.*, **33**, 452).—Twelve grams of the powdered beans is introduced into a 200 c.c. flask and 80 grams of ether and 40 grams of chloroform are added; after half an hour 10 c.c. of 10 per cent. ammonia is added, and the whole is shaken at intervals for half an hour. After adding 15—20 c.c. of water and thoroughly shaking, 100 c.c. of the ethereal mixture is poured off into a separating funnel and shaken with 50 c.c. of 0·5 per cent. hydrochloric acid, the shaking being repeated with another 25 c.c. The acid liquid is drawn off, and after adding excess of ammonia, it is agitated thrice with 30 c.c. of chloroform mixed with 10 c.c. of ether. This, on evaporation, yields the alkaloids from 10 grams of the beans. L. de K.

Separation of the Proteids of Milk. By A. Schlossmann (*Zeit. physiol. Chem.*, 1896, **22**, 197—226).—See this vol., ii, 62.

Estimation of Albumin in Urine. By Georges (*J. Pharm.*, 1896 [6], **4**, 108—110).—Mercier (*J. Pharm.*, [6], 515) has shown that in order to obtain accurate results the urine should be diluted with water, so that the quantity taken for analysis does not contain more than 0·1 gram of albumin. When much water has been added, the albumin shows a tendency to redissolve; this the author proves experimentally to be due to the dilution of the salts present in the urine.

He suggests a method of analysis in which a saturated solution of magnesium sulphate is used as a precipitant. M. W. T.

New Process for Estimating Albumin in Urine. By E. Riegler (*Chem. Centr.*, 1895, i., 332; from *Wien. Med. Bl.*, 1895, 761).—Ten grams of asaprol is dissolved in 100 c.c. of water, and 10 c.c. of hydrochloric acid and 5 c.c. of this solution are added to 50 c.c. of urine, and the whole heated to 60°. The precipitate is collected, washed with about 150 c.c. of water, pressed dry between filter-paper, and finally dissolved in 25 c.c. of N/10 potash. The difference in the refractive index of this solution and that of the potash by itself serves as a measure for the estimation of the albumin. Divided by 540, the amount of albumin in 50 c.c. of urine is obtained. If the urine is rich in albumin, a smaller quantity must be taken; if poor, a larger amount. (Compare Abstr., 1895, ii, 542.) L. de K.

General and Physical Chemistry.

Refraction and Density. By ISIDOR TRAUBE (*Ber.*, 1896, **29**, 2732—2742).—The expression $V_m = m/d = \Sigma nC + Cov = \Sigma nC + 25\cdot9$ (see Abstr., 1896, ii, 235) was termed by Kopp the apparent molecular volume, but the author prefers to call it the molecular vibration volume; it is composed of the true molecular volume ΣnC, which the author terms the atomic nucleus volume, and the molecular covolume *Cov.* The values of V_m are obtained from density determination, whilst an expression for the value of ΣnC is given by the Clausius-Mosotti theory of dielectrica; if v is the actual volume occupied by spherical molecules, k the dielectricity constant, and μ the refractive index for infinite wave-length,

$$v = (k - 1)/(k + 2) = (\mu^2 - 1)/(\mu^2 + 2),$$

the fraction of unit space actually occupied by a molecule is $\Sigma nC/V_m$, and it should be proportional to $(\mu^2 - 1)/(\mu^2 + 2)$ if the argument be valid. The values of $\Sigma nC\ (\mu^2 + 2)/V_m\ (\mu^2 - 1)$ have been calculated for a long series of saturated organic compounds, and are constant within very narrow limits, the mean values being 3·53 for Cauchy's constant A, 3·44 for the D line, and 3·460 for H_α; the values of ΣnC are calculated from the atomic nucleus volumes C = 9·99, H = 3·1, and O = 5·5. Consequently, the vibration volumes of the atoms calculated from molecular weight and density are equal to the atomic nucleus volumes or atomic refractions multiplied by constants which vary within narrow limits with the wave-length of the light.

The quantity $\mu - 1$ is the "loss of time" experienced by a ray in traversing a thickness of the substance, instead of an equally wide vacuous space which is traversed in unit time. The loss of time is also very strictly proportional to that fraction of the space filled by a substance which represents the molecular nucleus volume, so that $\Sigma nC/V_m\ (\mu - 1)$ is practically constant; this quantity has the mean values 2·086 for H_α, and 2·073 for D, and knowing the density of a given substance, it is possible to calculate with fair approximation the refractive indices for these rays. It is evident that the two above expressions involving ΣnC, V_m and functions of μ are independent of the temperature.

On dividing the atomic vibration volumes stated above by 2·086 or 3·460, the atomic refractions for H_α of the corresponding atoms for the Gladstone, or the Lorenz and Lorentz, formula respectively are obtained; the numbers thus got for the simple formula agree more closely with the numbers in use than do those for the theoretical formula. By applying the formula $\Sigma nC\ (\mu^2 + 2)/V_m(\mu^2 - 1)$ to unsaturated compounds, it is possible to calculate the increments of molecular refraction due to double linkings between the carbon atoms with very fair approximation. W. J. P.

Action of Light on Dyed Colours. Report of British Association Committee, Section B, Liverpool, 1896 (*Chem. News*, 1896, **74**,

205—207, 218).—The report refers to blue and green colouring matters on wool and silk exposed to light under glass with free access of air and moisture, and examined by comparison with standards at various intervals; a very large number of samples were examined and the general results are tabulated under five classes:—I, Very Fugitive; II, Fugitive; III, Moderately Fast; IV, Fast, and V, Very Fast Colours. Interesting comments and notes are also given. D. A. L.

Cadmium Standard Cell. By WILHELM JAEGER and R. WACHSMUTH (*Ann. Phys. Chem.*, 1896, [2], **59**, 575—591).—The use of cadmium in place of zinc for the construction of standard cells of the Clark type has been proposed on account of the reduction that is thus attained in the temperature coefficient of the cell. The authors have submitted this point to further investigation, and have also ascertained the ratio of the E.M.F. of the cadmium cell to that of the Clark cell, and the influence of impurities and of time on the constancy of the cadmium cell. The cell is best made of the usual H pattern, with electrolytically amalgamated platinum electrodes sealed through the glass. In place of pure cadmium, an amalgam of 1 part by weight of cadmium to 6 parts of mercury is used (m. p. 60°). The mercurous sulphate is mixed with crystals and a concentrated solution of cadmium sulphate and some mercury to a thick paste, and this paste is placed over the mercury of the positive pole. The negative pole (1Cd : 6Hg) is covered with a layer of cadmium sulphate crystals, and the rest of the cell is then filled with a concentrated solution of cadmium sulphate. The E.M.F. of this cell at 20° is 1·019 volt. The change in E.M.F. with change in temperature between 5° and 25° is expressed by the equation

$$E_t = E_{20} - 3{\cdot}8 \times 10^{-5}(t-20) - 0{\cdot}065 \times 10^{-5}(t-20)^2,$$

and is, therefore, for 1°, only about $\frac{4}{1000}$ per cent. In the effect of the influence of impurities and in durability, the cadmium cell was found to be in no way inferior to the Clark cell. H. C.

Heat of Formation of Lithium Hydride. By ANTOINE GUNTZ (*Compt. rend.*, 1896, **123**, 694—696. Compare Abstr., 1896, ii, 359).—The heat of formation of lithium hydride was calculated from the heats of dissolution of the hydride and of the metal itself in water.

Heat of dissolution of lithium hydride in water at 18° = +31·6 Cal.

Heat of dissolution of lithium in water at 18° = +53·2 Cal.

Therefore, Li solid + H gas = LiH solid = +21·6 Cal., a number which explains the stability of the compound.

The fact that the above value for the heat of dissolution of lithium in water is much greater than that obtained by Thomsen, namely, +49·08 Cal., is attributed by the author to the much greater purity of the metal used by him. The heats of formation of lithium compounds deduced from Thomsen's number are accordingly too low. Lithium hydride melts at 680°, at which temperature its tension of dissociation is about 27 mm. At ordinary temperatures, dry chlorine has no action on it; when heated in a current of that gas to a dull red heat, it burns, giving lithium chloride and hydrogen chloride. At a red

heat, hydrogen chloride acts on it, forming lithium chloride and hydrogen.

It reacts slowly with absolute alcohol, but is without action on dry benzene, toluene, or petroleum, at ordinary temperatures. Lithium hydride differs markedly in its properties from the hydrides of sodium and potassium. A. C. C.

Thermochemistry of Cyanamide. By PAUL LEMOULT (*Compt. rend.*, 1896, **123**, 559—562).—The cyanamide used was prepared by the action of mercuric oxide on thiocarbamide, and its molecular weight was determined by cryometric observations on its solution in acetic acid. Combustion in the calorimetric bomb gives 4090 Cal. as the heat of combustion of 1 gram; the molecular heat of combustion is, therefore, 171·78 Cal. at const. vol., and 171·5 Cal. at const. pressure, the heats of formation from its elements being −8·4 Cal. and −8·2 Cal. respectively. Its heat of dissolution in water is −3·59 Cal., and hence its heat of formation in solution is −12·0 Cal., a result which explains the greater stability of the compound when in the solid state.

From these data, it follows that the action of mercuric oxide on thiocarbamide develops +25·2 Cal., whilst the conversion of cyanamide in dilute solution into carbamide would develop +20·2 Cal.

The addition of dilute acids to solutions of cyanamide causes no thermal disturbance, but the heat of neutralisation by potassium hydroxide (one molecular proportion) is +3·79 Cal., and by sodium hydroxide +3·6 Cal. In either case, the addition of a second molecular proportion of alkali causes a slight development of heat, but a third proportion has no effect. The heat of neutralisation by ammonia is +1·38 Cal. It follows that in aqueous solution cyanamide behaves as an acid, the energy of the acidic function being comparable with that of hydrocyanic acid. It would seem also that there is a difference between the functions of the two replaceable atoms of hydrogen.

C. H. B.

Thermochemistry of Hexamethylenetetramine and its Nitroso-derivatives. By MARCEL DELÉPINE (*Compt. rend.*, 1896, **123**, 650—653).—The heat of combustion of pure hexamethylenetetramine, determined by burning in the calorimetric bomb, is 1006·53 Cal. (const. press.), and its heat of formation from its elements −26·73 Cal.

Its heat of dissolution in water at 15° (1 mol. in 1·5 to 2·5 litres of water) is 4·8 Cal., from which the heat of formation of dissolved hexamethyleneamine is −21·93 Cal. In order to verify the accuracy of the latter number, it was employed in calculating the heat of formation of hexamethylenetetramine dinitrate, and the result, 92·3 Cal., compared with that obtained by direct experiment +92·94 Cal.

It is incidentally remarked that hexamethylenetetramine dinitrate (47·37 per cent. HNO_3) gives, on combustion, very little nitric acid.

First Nitroso-derivative, $(CH_2)_5(NO)_2N_4$.—Heat of combustion (const. press.) = 872·28 Cal., from which its heat of formation (cryst.) is found to be −55·78 Cal.

Second Nitroso-derivative, $(CH_2)_4(NO)_4N_4$ (compare Abstr., 1889, 33).

—Heat of combustion (const. press.) = 745·96 Cal., from which its heat of formation is found to be − 91·76 Cal.

The replacement, therefore, of CH_2 by $(NO)_2$ diminishes considerably the heat of formation of these substances, and renders it strongly endothermic, the second substitution producing a greater diminution than the first. The nitroso-derivatives are much less stable than the base itself. A. C. C.

Dependence of the Dissociation of some Acids on Temperature and the Heat of Dissociation. By HANS EULER (*Zeits. physikal Chem.*, 1896, 21, 257—271).—Determinations of the conductivity were made by Kohlrausch's method in the case of benzoic, toluic, salicylic, metahydroxybenzoic, ortho- and meta-nitrobenzoic, and dichloracetic acids, at various temperatures between 10° and 50°, and at various dilutions. Interpolation formulæ were calculated which, in almost all cases, except with the sodium salts, were of the form $\lambda = a + bt - ct_2$, indicating the occurrence of a maximum (compare Jahn and Schröder, Abstr., 1895, ii, 203). From these values, the dissociation constants are calculated at the different dilutions and temperatures, the values from the different dilutions agreeing satisfactorily with one another, except in the case of orthonitrobenzoic acid and dichloracetic acid, where, however, the value at 0° was undoubtedly higher than that at 25°, results not in accord with those of Wildermann. In all cases, the dissociation constant is a function of the temperature, a maximum occurring for benzoic acid at about 35°, and for metahydroxybenzoic acid at about 28°. For orthotoluic acid, the values decrease continuously as the temperature rises, but increase for salicylic and metanitrobenzoic acids. Calculation of the heat of dissociation of the acids proved it to invariably increase with rise of temperature. In most cases, it is at first negative, the temperature at which zero is reached being that of the maximum dissociation, a relation indicated by the expression $Q = 0{\cdot}50804\ T^2.1/k.dk/dt.$ from which the values are calculated.

L. M. J.

The Determination of Molecular Weights. IV. By ERNST O. BECKMANN (*Zeits. physikal. Chem.*, 1896, 21, 239—256).—The paper contains further details of the apparatus and methods employed by the author. An electromagnetic stirrer is described, for use in freezing point determinations, whereby the apparatus can be kept completely closed and the entrance of moist air avoided, an important precaution when phenol or acetic acid are employed as solvents. A form of boiling point apparatus is described, small tetrahedra of platinum foil being recommended for the prevention of bumping; and the author states that in the Beckmann thermometers a *conical* junction of the capillary tube to the reservoir is necessary. Experiments are recorded indicating the availability of the apparatus as described, aniline, water, chloroform, ether, ethylic alcohol, and benzene being employed as solvents (comp. Abstr., 1895, ii, 154, 382; 1896, ii, 236). L. M. J.

Exact Cryometry: Application to Sodium Chloride Solutions. By FRANÇOIS M. RAOULT (*Compt. rend.*, 1896, 123, 475—478).

—The author has made several series of determinations of the freezing points of solutions of sodium chloride, using the apparatus previously described (*Compt. rend.*, 1896, **122**), but employing ether instead of carbon bisulphide. It was found that the temperature could be kept constant to 0·1° at any point between − 15° and the surrounding temperature for several hours. In the following table, P is the weight of salt in 100 grams of water; C, the apparent reduction when the converging temperature is 3·5° below the freezing point; C_0, the real reduction when the converging temperature and the freezing point coincide.

P	C_1	C_0	$C_1—C_0$	$C_0 \times 0·002$
5·850	3·4435	3·4381	0.0054	0·0068
2·859	1·6880	1·6839	0·0041	0·0034
1·400	0·8286	0·8267	0·0019	0·0017
0·690	0·4132	0·4111	0·0021	0·0008
0·341	0·2107	0·2093	0·0014	0·0004
0·176	0·1113	0·1111	0·0002	0·0002

$C_0 \times 0·002$ and $C_1—C_0$ are practically identical, and hence $C_1—C_0 = C_0 \times 0·002$ or $C_1 = C_0(1 + 0·002)$, and the general expression $C_1 = C_0(1 + q)$ previously arrived at (q having always a very small value) is experimentally verified for sodium chloride solutions.

The real and apparent molecular reductions can be calculated from the figures in the table; the limiting value is 38·05 for the former and 37·88 for the latter. The curves, with the observed reductions for abscissæ and molecular reductions for ordinates, are very similar in the two cases, and cut the axis of the ordinates at practically the same point, which corresponds with the limiting molecular reduction. The experiments with sodium chloride, therefore, confirm the author's previous conclusion that the temperature of the surroundings has no influence on the laws relating to the reductions of the freezing point of different solutions of the same substance.

The real molecular reductions given in the table correspond to a superfusion of 0·5°, and the absolute values, when the concentration is not altered by freezing, are obtained by multiplying the figures by 0·994. The limit molecular reduction for sodium chloride is then found to be 37·82, which is identical with that requiring complete ionisation.

The different results obtained by Ponsot (Abstr., 1896, ii, 411, 636) are attributable to insufficient agitation of the liquid, especially in a vertical direction. C. H. B.

Exact Cryometry : A Correction. By FRANÇOIS M. RAOULT (*Compt. rend.*, 1896, **123**, 631—632).—After some reference to an earlier paper (preceding abstract), it is remarked that, in the determination of the true depression of the freezing point, absence of radiation is not theoretically necessary, which is fortunate, since that condition is absolutely incapable of realisation, owing to the development of heat produced by the agitation of the liquid. A. C. C.

Expansion during the Dissolution of Ammonium Salts and of Sodium Thiosulphate. By HUGO SCHIFF and U. MONSACCHI

(*Zeits. physikal. Chem.*, 1896, **21**, 277—296).—The expansion occurring during the dissolution of ammoniacal salts was first determined, pyknometers of 25 c.c. and 50 c.c. capacity being employed. In the case of ammonium nitrate, the expansion (throughout referred to 100 parts of the mixed constituents) was found to vary from 4·0 for a 63 per cent. solution to 0·179 for a 4 per cent., with a minimum of 0·119 at 7 per cent. As the expansion may be due to a dissociation into ammonia and nitric acid, the effect of dissolution in dilute nitric acid was determined, but the expansion was found to be even greater than in aqueous solution, a result also obtained by dissolution in potassium nitrate and ammonium chloride solutions. The expansion may be fairly well calculated by assuming that a saturated solution of the ammonium nitrate is first formed, and then mixed with a solution containing the other salt and the remaining water. In methylic alcohol, however, a contraction of about 0·86 occurs for the saturated solution (14 per cent.). Ammonium chloride gave an expansion of 2·6 at 30 per cent. and 0·46 at 10 per cent., that of ammonium bromide being in each case slightly lower. In the case of ammonium iodide, however, contraction occurs, varying from 1·4 at 60 per cent. to 0·035 at 3 per cent., and is greater in alcohol than in water. Hydroxylamine hydrochloride gave an anomalous result, contraction first occurring reaching a maximum at from 10 to 15 per cent. with normal volume at 28 per cent., after which expansion occurs, whilst in the case of hydrazine hydrochloride a perfectly regular contraction obtains. Sodium thiosulphate gave results very similar to that of the hydroxylamine salt, the maximum contraction occurring at 40 per cent. and zero at 78 per cent., after which expansion occurs, the values being not quite concordant with those of Boisbaudran (Abstr., 1895, ii, 486), partly owing to the latter using a higher sp. gr. for the solid salt (1·752) than that obtained by the authors (1·734). L. M. J.

Laws of Irreversible Processes. By LADISLAUS NATANSON (*Zeits. physikal. Chem.*, 1896, **21**, 193—217).—A mathematical paper, unsuitable for abstraction, in which the author deduces expressions for the velocity of various irreversible processes, such as diffusion, heat conductivity, dissipation of electrical energy. L. M. J.

Relationship of the Rate of Diffusion to the Initial Concentration of Dilute Solutions. By W. KAWALKI (*Ann. phys. Chem.*, 1896, [2], **59**, 637—651).—Nernst has shown, as a consequence of the dissociation theory, that the rate of diffusion of dissolved substances should alter very little with the concentration when the solutions reach a certain degree of concentration. In former experiments (Abstr., 1894, ii, 345), the author found that with very small initial concentrations the values calculated for the diffusion coefficient k do not correspond with one another, and it was pointed out that the behaviour was probably due to convection currents. Careful experiments with dilute solutions of sodium acetate and carbamide have since served to confirm this view and support Nernst's conclusions. The diffusion coefficient, k_1 for dilute alcoholic solutions was also determined, and the ratio k_1/k found for sodium acetate = 2·19, and for carbamide = 1·79. H. C.

Determination of Isosmotic Concentrations. By SVEN G. HEDIN (*Zeits. physikal. Chem.*, 1896, **21**, 272—276).—Chiefly a controversial paper and a criticism of Köppe's results (Abstr., 1895, ii, 208). The author considers that errors occur in Köppe's work owing to (1) the use of salts which directly affect the blood corpuscles, (2) the use of standard solutions which are not actually isosmotic, whilst, further, he considers it necessary to defibrinate the blood employed.

L. M. J.

Explosive Properties of Acetylene. By MARCELLIN P. E. BERTHELOT and PAUL VIEILLE (*Compt. rend.*, 1896, **123**, 523—530).—When acetylene under ordinary pressure is subjected to the action of an electric spark, a red-hot wire, or a discharge of fulminate, the decomposition of the gas does not extend beyond the immediate neighbourhood of the source of decomposition, but under pressure the results are different, and when the pressure exceeds two atmospheres the gas shows the ordinary properties of explosive mixtures. Under these conditions, if decomposition is produced at any point by one of the methods indicated, it very rapidly spreads through the whole mass of the gas, which is thereby resolved into hydrogen and bulky pulverulent carbon. Under an initial pressure of 21 kilos. per square cm., the pressure developed by the decomposition is 10 times as great, and the change is complete in 0·018 of a second. The ratio of the final to the initial pressure decreases, and the time required for complete decomposition increases, the lower the pressure. Even with an initial pressure of 21 kilos. per square cm., the rate of propagation of the change is much below the velocity of the explosive wave in the oxyhydrogen mixture. The calculated temperature of decomposition is 2750°, and the calculated pressure 11 times as great as the initial pressure. The observed pressure agrees fairly well with the calculated.

Liquefied acetylene decomposes in the same way as the gas; with 18 grams of the liquid in a bomb of 48·96 c.c. capacity, the final pressure was 5,564 kilos per square cm., and under these conditions the explosive force is nearly equal to that of guncotton. The decomposition of the liquid is, however, relatively slow when excited by simple ignition. When the bomb contains both liquid and gas, there is a change in the curve of pressure which indicates two distinct phases of the explosion, one most probably corresponding with the decomposition of the gaseous part, and the other, which lasts longer and raises the pressure much higher, to the decomposition of the liquid portion.

Mere shock, such as is caused by a fall from a considerable height, seems incapable of causing the explosion of either compressed or liquefied acetylene. If the vessel breaks there is still no explosion in the case of the compressed gas; but if the vessel contains liquid acetylene, the fracture is followed after a short interval by an explosion. The latter, moreover, differs essentially from the explosive decomposition of the gas, and is not accompanied by the separation of free carbon; it results from the admixture of air with the acetylene, and the ignition of this mixture by sparks that result from the friction of the breaking metal.

If, however, liquid acetylene is decomposed by the discharge of a

small quantity of fulminate contained in the same vessel, violent detonation takes place, and the fragments of the vessel have the appearance of those produced by a true explosion. All the fragments are covered with the carbon liberated from the gas.

In the action of small quantities of water on excess of calcium carbide in a closed vessel, there may be sufficient local elevation of temperature to initiate the decomposition of the whole of the compressed gas. This local elevation of temperature may also produce polymerides, which are themselves endothermic. Other causes of dangerous local heating are too rapid compression, or the local pressure that arises when the gas is allowed to escape very suddenly from a vessel in which it is highly compressed. The precautions needed to prevent accidents arising from these causes are obvious. C. H. B.

Influence of Pressure on the Inversion Constants of some Acids. By O. STERN (*Ann. Phys. Chem.*, 1896, [2], **59**, 652—663).—The change in the conductivity of electrolytes with an increase in the external pressure has been accounted for on the supposition that the rise in pressure produced an increase in the electrolytic dissociation. Röntgen found, however, that an increase in the pressure does not accelerate, but retards, the rate of inversion of cane sugar by hydrochloric acid. The author has extended Röntgen's observations, and finds that the rate of inversion of solutions containing 23 grams of cane sugar per 100 c.c., and varying amounts of hydrochloric, sulphuric, or oxalic acid, is always reduced when the external pressure is increased from 1 to 500 atmospheres. The influence of the pressure on the rate of inversion is smaller, the smaller the amount of acid added. If the inversion is brought about by phosphoric or acetic acid, the reverse is true, as pressure here increases the rate of inversion, and this increase is the greater, the greater the amount of acid added. The rate of inversion decreases somewhat as the concentration of the sugar solutions is decreased, but the change in the rate of inversion with the pressure remains about the same. A rise in temperature of about 10° produces a very marked increase in the rate of inversion, but here, again, the effect of an increase of pressure remains about the same. H. C.

Crystal Symmetry. By VIKTOR VON LANG (*Zeits. physikal. Chem.*, 1896, **21**, 218—224).—The author draws attention to the simple method which he used many years ago in his *Lehrbuch der Krystallographie* (Wien, 1866) for deducing the thirty-two possible types of crystal symmetry from fundamental crystallographic laws; the argument is restated and its simplicity urged in favour of its more general use. A system of nomenclature for the thirty-two crystal systems is proposed, which has the advantage over many others that the names indicate immediately the prominent characteristics of the types of symmetry they are intended to describe. W. J. P.

Atomic Weights of the Elements. By DELAUNEY (*Compt. rend.*, 1896, **123**, 600—603).—The author arranges the elements in four groups, according as their atomic weights, expressed by the nearest

whole numbers, are 0 + a multiple of 4, 1 + a multiple of 4, 2 + a multiple of 4, or 3 + a multiple of 4. The first group is the largest, and the elements in it can be arranged in three columns, the successive members in each of which differ from the element at the top (C (12), Ce (92), or x (172) by 4, 8, 4, 4, 8, 4, 4, 4, 4, 24. There are gaps due to undiscovered elements or to inaccurate determinations of known elements. The next largest class contains elements whose atomic weights are 3 + a multiple of 4, and here there are two columns, the successive members of which differ from the first in the same way as in the first group, but only three known elements are contained in the second column. On the other hand, several elements that properly belong to this group do not fit into the columnar arrangement. The group 2 + a multiple of 4 contains eight elements which, starting from the first, helium, increase by 12, 56, 20, 16, 20, 56, 12, whilst the three elements in the groups 1 + a multiple of 4 increase after the first (Be) by 56 and 20. A certain number of the less known elements do not fit into any of these groups. C. H. B.

Hypothesis of the Atomic Motion of the Elements and their Genesis. By FLAVIAN FLAWITZKY (*Zeits. anorg. Chem.*, 1896, **12**, 182—187).—The author advances the hypothesis that the atoms of an element move in curves which lie in planes parallel to one another. The atoms of different elements move in planes which are inclined at certain definite angles to one another. The orientation of the motion determines the character of the element, and can be regarded as due to the influence of some selective dualistic force, such as electricity, in the formation of the element. H. C.

A New Form of Turbine for Use in Laboratories. By GEORGE F. JAUBERT (*Bull. Soc. Chim.*, 1896, [3], **15**, 9—10).—The author describes a new form of turbine for use in laboratories supplied with water under high pressure. The turbine is designed for carrying out operations on a moderate scale. No details are given with regard to construction. M. W. T.

Inorganic Chemistry.

Slow Oxidation of Hydrogen and Carbon. By H. HIRTZ and VICTOR MEYER (*Ber.*, 1896, **29**, 2828—2831. Compare this vol., ii, 19).—It is improbable that ozone was formed in the earlier experiments (*loc. cit.*), as the gas evolved when dilute sulphuric acid acts on potassium permanganate is quite inert, and ozone appears to be produced only when the concentrated acid is employed.

Morse, Hopkins, and Walker have shown (Abstr., 1896, ii, 475) that, under certain conditions, finely divided manganese dioxide effects the reduction of potassium permanganate, oxygen being liberated. These conditions, however, were not those employed in the above

experiments, and again only in the acidified permanganate was any appreciable residue observable. Later experiments have shown that acidified permanganate solutions in contact with manganese dioxide yield only 12·5 per cent. of the volume of gas obtained when hydrogen is present,

The difference in volume between the amount of oxygen obtained when the permanganate solution is quiescent, and when it is strongly agitated, has suggested the idea that the action is a reversible one; experiments made with the object of observing any absorption of oxygen under the conditions employed have given negative results, thus rendering the suggestion improbable. A. L.

Purification of Water by Distillation. By GEORGE A. HULETT (*Zeits. physikal. Chem.*, 1896, **21**, 297—301).—The author recommends the use of a condenser containing an inner tube of platinum, narrowed slightly at the lower end, and with the upper end projecting about 15 cm. into the neck of the retort employed for the distillation. The space between the platinum tube and the neck of the retort is packed with asbestos, and by this means only the water actually condensed in the platinum tube is collected. Ordinary distilled water which had been allowed to remain over potassium permanganate or potassium dichromate and sulphuric acid, when distilled over barium hydroxide in this apparatus, gave a distillate of speedily diminishing conductivity, the value $0·76 \times 10^{-10}$ being reached before one-fourth of the water had distilled. No barium hydroxide appears to be carried over, but, if it is not employed, sulphuric acid may occur in the distillate.

L. M. J.

Nitrites in the Air. By GEORGE DEFREN (*Chem. News*, 1896, **74**, 230—231).—Re-distilled water, free from ammonia, nitrites, and nitrates, was exposed to the air in well-ventilated rooms, in porcelain evaporating dishes 15 cm. in diameter; each dish contained 100 c.c. of the water, the superficial area exposed being 95 sq.cm. The water was examined at intervals for nitrites, the quantity being computed by comparison with a standard solution of potassium nitrite containing, per c.c., 0·0000001 gram of nitrogen as nitrite, the conditions as regards burning gas jets and lamps being noted. Under varying conditions, the quantity of nitrite, in terms of c.c. of standard, found, after one hour, was 2·5, 3·5 and 8; after two hours, 3·5, 8·5 and 13·5; after seventeen hours, in the last instance, 84·2; and after nineteen hours, in the first and second instance, respectively 57·2 and 72·7. The results show that, where gas is burning, nitrites exist in the air even in well-ventilated rooms, and that water absorbs these nitrites in quantities increasing with the time of exposure to the polluted air. D. A. L.

Tetrametaphosphimic Acid. By HENRY N. STOKES (*Amer. Chem. J.*, 1896, **18**, 780—789. Compare this vol. ii, 28.)—*Tetrametaphosphimic acid*, $P_4N_4O_8H_8 + 2H_2O$, is best prepared by the action of water on tetraphosphonitrilic chloride, $P_4N_4Cl_8$, dissolved in ether free from alcohol. Chlorhydrins are formed as intermediate products, but remain dissolved in the ether, the acid crystallising in needles from

the aqueous portion. The oily chlorhydrins, when separated, and warmed with dilute hydrochloric acid, yield the acid, crystallising in colourless needles. One hundred parts of water at 20° dissolve 0·64 part of the crystallised acid; it is somewhat more soluble in boiling water, but insoluble in alcohol. Boiling alkaline solutions cause no evolution of ammonia, and heating with moderately strong hydrochloric or nitric acids brings about but little decomposition. The water of crystallisation is not given off in a vacuum over sulphuric acid, but when heated at 100° the crystallised acid loses weight rapidly, although the theoretical loss is never reached owing to intramolecular changes, in which a portion of the water takes part. It forms three series of salts, $P_4N_4O_8H_6M'_2$, $P_4N_4O_8H_4M'_4$, and $P_4N_4O_8M'_8$.

Dipotassium tetrametaphosphimate, $P_4N_4O_8H_6K_2$, was prepared by adding excess of acetic acid to a solution of the acid in cold, dilute caustic potash. On warming, the salt is deposited as a heavy, sandy powder, consisting of microscopic, thick, rectangular (? quadratic) prisms with basal planes; it is very sparingly soluble, even in boiling water. The *tetrapotassium* salt, which is very soluble, forms large, flat, obliquely-terminated plates. The *tetrasodium* salt, $P_4N_4O_8H_4Na_4 + 2\frac{1}{2}$ (?) H_2O, forms obliquely-terminated, flat prisms; it is sparingly soluble in cold, but readily in hot water.

The *tetrammonium* salt, $P_4N_4O_8H_4(NH_4)_4 + 4H_2O$, is obtained by treating the acid with strong ammonia, and usually forms well-developed, flat, monoclinic prisms; it dissolves readily in water, but with difficulty in strong ammonia. The *diammonium* salt, $P_4N_4O_8H_6(NH_4)_2$, is precipitated from a solution of the neutral salt on strongly acidifying with acetic acid and warming; it forms four- and six-sided prisms (? tetragonal), and is very sparingly soluble, even in boiling water. The *barium* salt, $P_4N_4O_8H_4Ba_2 + 2H_2O$, forms microscopic needles. No definite results were obtained in the attempt to prepare a magnesium salt. The *manganese* salt forms characteristic, pink, rectangular plates. Ferric chloride when added to a dilute solution of the neutral ammonium salt gives, on warming, a white, amorphous precipitate soluble in much warm hydrochloric acid. The *tetra-silver* salt, $P_4N_4O_8H_4Ag_4$, is obtained on adding a solution of silver nitrate to one of the free acid. When the precipitation takes place in the cold, the salt is granular or amorphous, but is crystalline when formed in hot solutions. The *octo-silver* salt, $P_4N_4O_8Ag_8$, is obtained as a yellowish, flocculent precipitate when an ammoniacal solution of the acid is added to an excess of silver nitrate; on the other hand, a solution of a neutral tetrametaphosphimate added to an ammoniacal silver nitrate solution, produces a white, flocculent precipitate. If a solution of the latter in ammonium nitrate is boiled, an orange-yellow, semicrystalline precipitate is formed. The white and the yellow compounds give on analysis almost the same numbers, and are regarded as tautomeric forms corresponding with the acids $[PN(OH)_2]_4$ and $(PO{\cdot}NH{\cdot}OH)_4$. The author discusses the probable constitution of tetrametaphosphimic acid, and calls attention to the fact that, in its general properties, it differs markedly from the trimetaphosphimic acid previously described by him. A. C. C.

Uniformity of the Distribution of Argon in the Atmosphere. By TH. SCHLŒSING, JUN. (*Compt. rend.*, 1896, **123**, 696—697. Compare Abstr., 1896, ii, 166 and 219).—The author has made determinations of argon in samples of air collected in places widely separated, and taken at various distances (a few metres to 2,275 m.) from the earth's surface. His numbers, which are very concordant, show that argon is uniformly distributed in the atmosphere, and that every 100 volumes of the mixed nitrogen and argon contain 1·192 volumes of the latter gas. This is in strict accordance with his previously published number.

A. C. C.

A Method of Preparing Double Silicates of Potassium and other Metals. By ANDRÉ DUBOIN (*Compt. rend.*, 1896, **123**, 698—700).—By dissolving a mixture of magnesia and silica in fused potassium fluoride and then submitting the product to prolonged fusion with potassium chloride, the author has obtained both a double silicate of magnesium and potassium, and two compounds containing fluorine in addition,

$$4KF,SiO_2 + 3MgO,2K_2O,10SiO_2 \text{ and } 2MgF_2,SiO_2 + 4(K_2O,MgO,3SiO_2)$$

(see Abstr., 1895, ii, 351). Beryllium oxide dissolves in fused potassium fluoride, and when submitted to the treatment described above, gives a crystalline product which appears to be homogeneous, but really consists of a mixture of isomorphous compounds. These are not analogous in composition to the double silicates of magnesium and potassium, but vary between $2K_2O,3BeO,7SiO_2$ and $2K_2O,3BeO,5SiO_2$; moreover, no double silicates containing fluorine could be prepared as in the case of magnesium. On adding baryta to fused potassium fluoride containing dissolved silica, a crystalline double silicate having the formula $K_2O,2BaO,3SiO_2$ (sp. gr. = 3·78) was obtained. If this mixture is fused with potassium chloride, three compounds are formed, the principal one having the formula $K_2O,7BaO,8\ SiO_2$, but containing a little fluorine. Double silicates could not be prepared in the case of calcium, the products always containing chlorine or fluorine; mixtures of crystalline products were obtained, only one of which, having the formula $4KF + K_2O,5CaO,6SiO_2$, could be isolated. A. C. C.

Rubidium Dioxide. By HUGO ERDMANN and PAUL KÖTHNER (*Annalen*, 1896, **294**, 55—71).—The authors have investigated the inflammable nature of metallic rubidium, in order to ascertain whether the spontaneous combustion of this substance on exposure to air, observed by Bunsen in 1863, is due to the influence of oxygen or of moisture.

The methods hitherto adopted for the production of metallic rubidium are very unsatisfactory, and the authors describe a convenient and safe process by which 85 per cent. of the theoretical quantity of the metal may be obtained from rubidium hydroxide. A seamless iron tube, of 15 mm. bore, 1 metre in length, having walls 3 mm. thick, is bent at an angle of 125° about 15 cm. from one end, fitted at the elbow with a loose plug of clean, long, steel shavings, and heated to redness while a current of hydrogen is passed through it; 20 grams of

freshly fused, anhydrous rubidium hydroxide is rapidly crushed to a coarse powder with magnesium filings (10 grams), in a warm mortar, and transferred to the long arm of the tube. This is placed in a small combustion furnace, with the short arm dipping beneath the surface of paraffin oil in a porcelain vessel, a gentle current of hydrogen, free from arsenic and dried by means of sulphuric acid and phosphoric anhydride, being passed through the tube; the temperature is cautiously raised, the application of heat being interrupted as soon as the increase in the current of gas indicates that the action has begun. When hydrogen is no longer evolved from the rubidium hydroxide, the temperature of the tube is raised to a red heat, and after half an hour the metal distils over, 14 grams being obtained from the quantity of hydroxide mentioned. When obtained in this manner from rubidium hydroxide prepared from ferric rubidium alum (Erdmann, Abstr., 1894, ii, 351), the metal is in a highly purified condition, and forms a convenient source of salts required for physical investigations; it melts at 38·5°, and has a sp. gr. = 1·5220 at 15°.

Rubidium dioxide, RbO_2, is obtained by the action of dried oxygen on the metal at common temperatures. In view of the fact that burning rubidium attacks glass, porcelain, platinum, silver, and rubidium chloride, it is necessary to allow the metal to fall into an aluminium dish which lies in a small glass flask filled with nitrogen; the whole apparatus is then weighed, and when the metal is converted into oxide, it is again filled with nitrogen, and weighed. The metal quickly melts when a stream of oxygen plays on it, and becomes ignited if the current of gas is not checked; when the oxidation proceeds in a normal manner, however, the metal preserves for some time the appearance of molten gold, but finally swells and becomes black, and then ceases to absorb the gas. On raising the temperature to 500°, it again begins to absorb oxygen, probably owing to the presence of metallic particles previously protected by oxide from the action of the gas, the volume becomes reduced, and a viscous, black liquid is produced; after this stage has been reached, no more oxygen is absorbed, and on cooling the apparatus, the oxide crystallises in dark brown plates. The authors have obtained no evidence of the existence of other oxides of rubidium, and the dioxide they describe may be heated at a high temperature without losing or absorbing oxygen; it acts violently on water, however, yielding rubidium hydroxide and hydrogen peroxide, oxygen being liberated. When rubidium dioxide is gently heated in an atmosphere of hydrogen, rubidium hydroxide, water, and oxygen are produced, a result which the authors attribute to the intermediate formation of hydrogen peroxide, in accordance with the equation $2RbO_2 + 2H_2 = 2RbOH + H_2O_2$; if the action proceeds at too high a temperature, violet light is developed, less water is formed, and the aluminium dish is corroded, rubidium aluminate, $RbAlO_2$, being produced.

It is convenient to employ an aluminium dish for the preparation of rubidium dioxide, because this metal is not wetted by molten rubidium, and it also resists the action of the fused dioxide at temperatures below 500°.

M. O. F.

Double Salts of Rubidium. By HUGO ERDMANN and PAUL KÖTHNER (*Annalen*, 1896, **294**, 71—79. Compare Abstr., 1894, ii, 351).—Ferric rubidium, ferric ammonium, and ferric potassium alums melt respectively at 53°, 43—44°, and 33°, and comparison of rubidium double salts with the analogous ammonium salts reveals the fact that ammonium more closely resembles rubidium than it does potassium.

Rubidium magnesium phosphate, $RbMgPO_4 + 6H_2O$, separates immediately on adding a warm solution of magnesium chloride to a mixture of rubidium chloride and disodium phosphate dissolved in water, the amorphous precipitate rapidly becoming crystalline; it is decomposed by silver nitrate, but resists the action of boiling water.

Hydrogen rubidium magnesium carbonate, $HRbMg(CO_3)_2 + 4H_2O$, is obtained by saturating an aqueous solution of rubidium carbonate with carbonic anhydride, and heating the liquid with magnesium carbonate during 5 minutes at 60°, a current of carbonic anhydride being passed through the liquid meanwhile; the filtered liquid deposits minute, transparent rhombs, having the edges flattened. The salt effloresces in a few days when exposed to air, and in this respect resembles hydrogen ammonium magnesium carbonate, whilst the potassium salt may be preserved for years without undergoing change.

Lead rubidium chloride, $PbRb_2Cl_6$, is obtained under the conditions observed by Friedrich, in preparing the analogous ammonium salt (Abstr., 1893, ii, 415); it is a yellow, crystalline powder, which closely resembles lead ammonium chloride. Concentrated sulphuric acid acts on it, liberating hydrogen chloride, and precipitating lead tetrachloride as an oil (compare *loc. cit.*), whilst the dilute acid converts the metals into sulphates, and liberates chlorine. Rubidium chloride may be precipitated almost quantitatively from its solution in methylic alcohol saturated with chlorine by adding a solution of lead tetrachloride, the precipitate being washed with 80 per cent. alcohol. Lead potassium chloride is much less stable than the rubidium salt, and evolves chlorine when dried in the air; the same change takes place when the rubidium salt is heated, the tetrachloride, $PbRb_2Cl_4$, being produced. The rubidium salt is also indifferent towards dilute hydrochloric acid and 96 per cent. alcohol, the potassium salt being decomposed by both agents; the changes produced under the influence of water and ammonia are less rapid than those which the potassium salt undergoes. In spite of these differences in behaviour, the estimation of rubidium in presence of potassium by means of lead tetrachloride is inaccurate; this agent, however, may be employed for the production of purified rubidium chloride from a solution containing 2 per cent. of potassium chloride.

Rubidium salts also resemble ammonium salts in respect to their volatility, and it is not possible to remove ammonium chloride from rubidium chloride by application of heat, without loss of the rubidium salt. Traube has shown that the atomic solution volume of rubidium is equal to that of ammonium (Abstr., 1895, ii, 70). M. O. F.

Electrolytic Silver Peroxide. By OTTOKAR ŠULC (*Zeit. anorg. Chem.*, 1896, **12**, 180—181).—The author points out that the product

of the electrolysis of silver nitrate which he recently described (Abstr., 1896, ii, 521), and to which the formula Ag_7NO_{11} was ascribed, may be regarded as a compound of silver peroxide and the heptoxide of nitrogen, and as being of the composition $7Ag_2O_2,N_2O_7$. The properties of the compound are consistent with this formula. H. C.

Peroxides in their Relationship to the Periodic System of the Elements. By AUGUSTO PICCINI (*Zeit. anorg. Chem.*, 1896, **12**, 169—179).—The author considers peroxides of the hydrogen peroxide type, such as BaO_2, TiO_3, and S_2O_7, in their relationship to the periodic system and to the question of the type of the highest oxygen compounds. As a general characteristic of oxides of this class may be quoted their reduction in acid solution by such oxidising agents as MnO_2, PbO_2, and $KMnO_4$. This distinguishes the peroxides from all other classes of oxides, and the peroxides are also distinguished by their lack of the acidic character that usually attaches to the higher oxides. These and other marked differences between the peroxides and the ordinary oxides of the water type lead to the conclusion that the peroxides cannot be regarded as compounds typical of the highest combining powers of the elements. H. C.

Double Bromides. By RAOUL VARET (*Compt. rend.*, 1896, **123**, 497—500).—The author has measured the heat developed on mixing aqueous solutions of mercuric bromide and of other metallic bromides capable of forming double salts of the type $2HgBr_2,MBr_2,nH_2O$, or $HgBr_2,MBr_2,nH_2O$, experiments being made with solutions of different degrees of concentration. As a rule, the development of heat is greater the more concentrated the solutions, and it is also increased by the presence of an excess of the soluble bromide. Similar experiments were made with cobalt and manganese bromides, and sodium and ammonium bromides.

The heats of formation in solution of the compounds of mercuric bromide with other metallic bromides are of the same order of magnitude for a given series of double salts, any differences that are observed being due to the unequal thermal effects resulting from dilution in different cases. The results lead to the conclusion that these double salts are derived from complex acids, such as $H_2Hg_2Br_6$ and H_2HgBr_4. The double salts formed by cobalt or manganese bromide with sodium or ammonium bromide are dissociated to a large extent on dialysis, and the thermal effects produced by mixing dilute solutions of their proximate constituents are very slight. C. H. B.

Aluminium Amalgam. By VICTOR BIERNACKI (*Ann. Phys. Chem.*, 1896, [2], **59**, 664—667).—A rod or wire of aluminium can be readily amalgamated by connecting it with one pole of a battery the other pole of which is connected with mercury, and then dipping the aluminium into the mercury and removing it again several times. The sparks formed each time at the connecting surfaces serve to heat the aluminium sufficiently to induce combination with the mercury. As the mercury in the amalgam appears to play the part of a catalytic agent, the smallest quantity of mercury at the end of an aluminium

wire will bring about oxidation of very considerable amounts of aluminium. H. C.

The Constitution of Inorganic Compounds. By ALFRED WERNER and ARTURO MIOLATI (*Zeit. physikal. Chem.*, 1896, **21**, 225—238).—The authors determined the electrical conductivity of various ammoniacal cobalt compounds with a view to the elucidation of their constitution. The conductivity of Jörgensen's dinitrotriaminecobalt chloride (Abstr., 1895, ii, 48) increased with the time, reaching a final constant value consistent with the presence of a univalent cation. The chlorine is, therefore, not present originally in the ion state, and hence cannot be united to the amine group, as Jörgensen supposed. The trinitrotriamine compound, $Co(NH_3)_3(NO_2)_3$, also contains no ion, the value for the conductivity being very low—1·6 at $v = 1000$, and totally different from that of the croceocobaltic nitrite,

$$NO_2 \cdot Co(NO_2)_2(NH_3)_4;$$

$\mu = 90$ at $v = 1024$. The nitritochlorotetraminecobalt chloride,

$$Cl \cdot Co\{NO_2Cl(NH_3)_4\},$$

originally gave the value $\mu = 68$ ($v = 240$), but after remaining for 70 minutes at 0°, the value had increased to 104, this being due probably to hydrolysis into $Co\{NO_2H_2O(NH_3)_4\}Cl_2$. The praseo-salts appear to undergo an analogous hydrolysis, from $Co\{(NH_3)_4Cl_2\}Br$ into $Co\{(NH_3)_4(H_2O)_2\}Cl_2Br$, as the conductivity increased in 40 minutes, from 116·6 to 332·1 with a final maximum $= 372$ ($v = 512$), the nitrite and nitrate exhibiting similar changes. The hydrogen sulphate, however, only gave an increase of from 373 to 439 ($v = 256$) so that, in this case, the final compound appears to be $Co\{(NH_3)_4H_2OCl\}SO_4$, the conductivity of which in 1/256 HCl solution is 439·7. The diaquodichlorodiamine salts, $Co\{(NH_3)_2(H_2O)_2Cl_2\}Cl$, also gave a marked increase after a time, corresponding with the ionisation of the two chlorine atoms. The sulphato-pentamine compounds contain the complex ion,

$$Co(NH_3)_5SO_4,$$

whilst a rapid increase of conductivity by dilution indicated hydrolysis to $Co(NH_3)_5H_2O$. The chloropentamine, aquopentamine, and aquochlorotetramine salts were also examined, and, as in the previous cases, the results indicated hydrolysis to aquo-salts, and were in complete accord with the author's views of the constitution of these compounds. (Abstr., 1894, ii, 407.) L. M. J.

Nickel Dioxide and its Acid Properties: Barium Nickelite. By EM. DUFAU (*Compt. rend.*, 1896, **123**, 495—497).—When an intimate mixture of nickelic oxide (85 parts) with barium oxide (155 parts) or barium carbonate (200 parts) is surrounded by barium oxide and heated for 10 minutes in the electric furnace with an arc from 60 volts and 300 ampères, a fused, grey mass is obtained with a crystalline fracture. It soon disintegrates when exposed to the air, and when rapidly treated with cold water, levigated, and finally washed and levigated with alcohol, it yields small, brilliant, dark-coloured crystals, which

are greenish-brown when powdered; sp. gr. = 4·8 at 20°; hardness a little above 4.

The crystals consist of barium dinickelite, $BaO,2NiO_2$, and are somewhat unstable. Cold water attacks them slowly and hot water rapidly. Hydrofluoric acid dissolves them with effervescence, and hydrochloric acid, with evolution of chlorine; nitric acid and ammonia, also dissolve and decompose them. Chlorine, bromine, and iodine attack the nickelite at a red heat, with formation of halogen salts of the metals, but oxygen has no action at bright redness. Sulphur, a little above its melting point, converts the nickelite into sulphides, with incandescence. Hydrogen fluoride and hydrogen chloride decompose it at a red heat, but fused neutral oxidising agents are without action on it.

It follows from these observations that nickel dioxide not only exists but has acid properties analogous to those of cobalt and manganese dioxides. Since nickelic oxide has no acid properties, it is probable that the oxide Ni_3O_4 has the constitution $NiO_2,2NiO$. C. H. B.

Diffusion of Sulphides through Steel. By EDWARD D. CAMPBELL (*Amer. Chem. J.*, 1896, **18**, 707—719).—Ferrous sulphide, cuprous sulphide, nickel sulphide (Ni_4S_3), and the product obtained by melting together ferrous sulphide and iron (? subsulphide of iron) are incapable of diffusing through steel bars heated to bright redness. When a mixture of 400 grams of ferrous sulphide with 13 per cent. of its weight of magnetic oxide of iron was melted, a product was obtained which the author regards as impure oxysulphide of iron, Fe_2OS; this was found to diffuse readily through red-hot steel bars and to have the property when mixed with cuprous sulphide, of carrying this with it. It is suggested that Fe_2OS, being at the temperature of the experiments an extremely mobile liquid (as shown by its rapid passage through the walls of the clay crucible used in its preparation), is able to diffuse through the steel on account of the porosity of the latter substance at a bright red heat. A. C. C.

Influence of Heat Treatment and of Carbon on the Solubility of Phosphorus in Steels. By EDWARD D. CAMPBELL and S. C. BABCOCK (*Amer. Chem. J.*, 1896, **18**, 719—723).—The authors have investigated the influence of the percentage of carbon in steel, and of the slow or sudden cooling of the latter on the solubility of the contained phosphorus. Estimations were made of the percentages of phosphorus (*a*) soluble in a neutral solution of mercuric chloride, (*b*) insoluble in mercuric chloride but soluble in 4 per cent. hydrochloric acid, and (*c*) insoluble in either of the above two liquids, and the following conclusions are arrived at:—(1) With very low carbon percentages, the rate of cooling of the metal has but little effect on the solubility of the phosphorus; (2) with increase of carbon, hardening diminishes the solubility, and (3) with high carbon percentages the solubility of the phosphorus is increased by slow cooling. It is suggested that these results point to the probable formation at a high temperature of a difficultly soluble compound of iron with carbon and phosphorus, which passes on slow cooling into an easily soluble one. A. C. C.

Bismuth Oxyiodide. By T. R. Blyth (*Chem. News*, 1896, **74**, 200).—The residue from the distillation of the double iodide of methylamine and bismuth with caustic soda, and the product of boiling bismuth oxyiodide, BiOI, with the same reagent, both have a composition corresponding with the formula $Bi_{17}I_3O_{24} = BiI_3,8Bi_2O_3 = 3BiOI,7Bi_2O_3$. It is a light, microscopically crystalline powder, with a very slight brown tint, soluble in dilute hydrochloric acid, not attacked by boiling water or alkalis, but is decomposed by nitric acid with liberation of iodine and by hydrogen sulphide with formation of sulphide. D. A. L.

Mineralogical Chemistry.

Advances in Mineralogical Chemistry. By BERNARD J. HARRINGTON (*Trans. Roy. Soc., Canada*, 1895, [2], 1, Sect. III, 3—17).—A presidential address, dealing generally with the separation, analysis, synthesis, and constitution of minerals. L. J. S.

Selenium associated with Gold and Bismuth: Graphitic Slate, and Water from N.S. Wales. By J. MILNE CURRAN (*J. and Proc. Roy. Soc., N.S.W.*, 1895, **29**, 404—408).—A slate from Mount Hope, N.S.W., containing native gold with bismuth oxide and carbonate, gave reactions for selenium; no sulphides were detected, but originally there was probably present an auriferous selenide or sulphide of bismuth.

A lustrous graphitic slate from Yalcogrin, on analysis, showed 12·5 per cent. of graphite.

The granite of the Wyalong gold-field is decomposed to a depth of 150 to 190 feet; the water supply from this decomposed rock gave, in grains per gallon: SiO_2, 37·268; Al_2O_3, 3·052; CaO, 43·540; MgO, 109·144; Na_2O, 551·236; K_2O, 6·188; SO_3, 192·430; Cl, 924·784; water of crystallisation, 209·300; Zn, trace; total (less O for Cl), 1868·55. Large quantities of soluble organic matter are present. Considering the origin of the water, there is a large amount of sodium chloride in it.

Some trachytes and other rocks from New South Wales are described. L. J. S.

Two New Mineral Substances from Broken Hill, N.S.W. By EDWARD F. PITTMAN (*J. and Proc. Roy. Soc., N.S.W.*, 1895, **29**, 48—51).—These substances, from the Australian Broken Hill Consols mine, are different from anything hitherto described, but they are only alteration products and mineral mixtures.

One of them is an alteration product of dyscrasite, which mineral it sometimes envelops; it is massive, and in sections shows a finely banded structure; the colour is greyish-brown, and the mineral is

sectile; the sp. gr. of one specimen is 4·9. Analysis by J. C. H. Mingaye gave the results under I, by H. P. White those under II.

	Moisture at 100°.	Comb. H_2O.	Ag.	Sb.	Cu.	Pb.	As.	Au.	CaO.
I.	0·56	4·04	47·46	16·87	0·11	0·62	trace	trace	3·78
II.	0·13	4·37	45·87	20·72	0·48	0·31	trace	—	4·25

	MgO.	Fe_2O_3.	Cl.	Insol.	O [diff.].
I.	1·17	2·11	13·69	1·01	[8·58]
II.	0·20	0·45	12·27	0·90	[10·05]

The silver exists as chloride and antimonide; the former is nearly all dissolved out from the powdered mineral by strong ammonia solution, leaving a residue which gave the following results on analysis :—

Ag.	Au.	Sb.	As.	Pb.	Cu.	Fe.	Ca.	Mg.
19·71	trace	35·12	trace	2·79	0·52	5·18	4·84	0·17

Insol.	Cl.	H_2O.	O.	Total.
5·20	0·14	6·01	19·69	99·37

The second substance is an alteration product of argentiferous galena; it is dark grey, has a cubical structure, and is sectile; the sp. gr. of one specimen is 6·38. The following analyses by Mingaye and White show that the composition is very variable.

	Moisture.	Ag_2S.	Cu_2S.	FeS_2.	$PbSO_4$.	PbS.	Insol.	Total.
I.	0·08	77·99	0·62	1·42	19·36	—	0·30	99·77
II.	—	76·62	0·32	0·45	19·80	0·50	1·60	99·73
III.	0·14	13·25	1·82	0·42	77·60	2·20	4·50	99·93
IV.	—	10·86	2·00	—	84·61	0·96	1·00	99·93

In II is also 0·44 per cent. of Sb_2S_3, and in IV 0·50 per cent. of Fe_2O_3. Ammonium acetate dissolves lead sulphate from the polished surface, leaving the silver sulphide in relief. L. J. S.

[Antimony Ochre, Celestite, Galena, Graphite, Tetrahedrite, Meymacite and Anthraxolite from Canada.] By G. Christian Hoffmann (*Ann. Report* (1894) *Geol. Survey, Canada*, 1896, N.S., 7, R., 1—68).—*Antimony ochre* occurs as an earthy incrustation, of a wine-yellow colour, on the stibnite of South Ham, Wolfe Co., Quebec. Analysis gave

Sb_2O_4.	As_2O_3.	Fe_2O_3.	Al_2O_3.	CaO.	MgO.	H_2O.	Quartz.	Total.
58·86	7·88	2·82	1·02	5·71	0·61	9·46	13·39	99·75

Celestite occurs, sometimes with calcite and galena, as a vein in crystalline limestone at Lansdowne, Leeds Co., Ontario; it is colourless, yellowish, or bluish, and semitransparent. Analysis shows it to be nearly pure strontium sulphate.

SO_3.	SrO.	BaO.	CaO.	Total.	Sp. gr
43·51	56·31	trace	0·11	99·93	3·958

Galena containing free sulphur, from West Kootanie, British Columbia, forms a coarsely crystalline aggregate with bright cleavage surfaces, and showing no visible signs of alteration. It readily takes fire, and burns with a pale blue flame. From the powdered mineral, carbon

bisulphide extracts sulphur, and ammonium acetate extracts lead sulphate. The mean of two very similar analyses is

S (free).	S (comb.).	SO_4.	Pb.	Sb.	Fe.	Zn.	Ag.	Total.
3·95	7·48	12·61	72·19	0·85	0·29	1·08	0·72	99·17.

This amount of SO_4 corresponds with 39·81 per cent. $PbSO_4$.

Graphite, from Marmora, Hastings Co., Ontario, is very finely granular, with uneven fracture, greyish black colour and dull lustre. It contains 72·13 per cent. of apparently amorphous graphite. The ash contains SiO_2, 36·0; Al_2O_3, 32·8; Fe_2O_3, 11·2; CaO, 2·0; MgO, 7·6 per cent.

Plumbiferous tetrahedrite, massive, with indistinct fibrous structure, from West Kootanie, British Columbia, gave the following results on analysis; sp. gr. 5·082.

S.	Sb.	As.	Cu.	Ag.	Pb.	Zn.	Fe.	Quartz.	Total.
20·59	26·81	0·22	21·03	10·64	8·91	5·91	0·88	5·57	100·56.

Meymacite occurs as a dull to bright yellow ochre with the scheelite of Marlow, Beauce Co., Quebec; it is a tungsten oxide with 7·2 per cent. of water. All the above analyses are by R. A. A. Johnston.

Anthraxolite, from a quartz vein in limestone and bituminous shale at Lake Petitsikapau, Ungava district, Labrador Peninsula, has an irregular structure, and is intermixed with quartz and other fragments; it gave on analysis

H_2O at 110—115°.	Loss on ignition in a closed vessel.	Fixed C.	Ash.	Total.
3·56	2·48	86·83	7·13	100·00.

The ash consists mainly of silica; another specimen gave 0·31 per cent. ash.

Various other mineralogical notes, chiefly relating to occurrences, are given. The report also includes analyses of coals, iron ores, nickeliferous pyrrhotite, calcareous marls, and waters, as well as the results of numerous gold and silver assays. L. J. S.

Bauxite and Emery. By A. LIEBRICH (*Zeit. prakt. Geol.*, 1895, 275—277).—It is pointed out that bauxite occurs in the younger rocks, whilst emery occurs in the oldest (gneisses, &c.); and that in their chemical composition the only important differences are the much larger amount of water in bauxite, and the presence of ferrous oxide (in the magnetite) in emery. Analyses of bauxite, calculated without the water, compare very closely with analyses of emery. This similarity of composition suggests that the two minerals may have the same origin; bauxite has been derived from silicates by decomposition, and the same must be true for emery, which has been brought into the present state by the action of water under pressure and at a high temperature. L. J. S.

Greenockite from Laurion. By ANASTASIOS C. CHRISTOMANOS (*Tsch. Min. Mitth.*, 1896, **16**, 360—361; and *Compt. rend.*, **123**, 62).—The calamine of Laurion, Attica, is very varied in colour and struc-

ture; a reddish, amber-yellow variety, which is vitreous and translucent, gave the following results on analysis.

ZnO.	CdO.	FeO.	CaO.	MgO.	Al_2O_3.	SiO_2.	S.	CO_2.	Total.
62·060	2·700	0·592	0·123	0·219	0·020	0·180	0·190	33·895	99·979

This corresponds with 92·57 per cent., $ZnCO_3$, 2·07 ZnO, 2·62 $CdCO_3$, and 0·85 CdS. Dusted over the surface, and in cavities, is a bright yellow, amorphous powder; the following analysis shows this to be greenockite.

Cd.	S.	Zn.	CO_2.
77·22	22·47	trace	trace

L. J. S.

Origin of Malachite. By EDGAR HALL (*J. and Proc. Roy. Soc., N.S.W.*, 1895, **29**, 416—419).—In an abandoned mine, in which the ore is cupriferous pyrites, the author has found malachite and azurite, and copper and iron sulphates; as the malachite and copper sulphate are both sometimes fibrous, it is suggested that the former is pseudomorphous after the latter. In dry seasons, the decomposition of the ore would give rise to an efflorescence of sulphates, which in wet seasons would be altered to carbonates by the action of carbonate solutions. L. J. S.

Blue Apatite from Montebras. By ADOLPHE CARNOT (*Bull. Soc. fran. Min.*, 1896, **19**, 214—215). In the tin mine of Montebras, Creuse, a darkish violet-blue apatite occurs in a very micaceous granite. With the cassiterite of this locality are several other phosphates, namely, amblygonite, montebrasite, wavellite, turquoise, and phosphates of iron and manganese. The apatite, on analysis, gave

P_2O_5.	F.	Cl.	CaO.	MgO.	MnO.	Fe_2O_3.	Quartz.	Total.
39·60	3·23	trace	50·45	trace	1·22	0·20	6·35	101·05

This corresponds with :—

$Ca_3P_2O_8$.	$Mn_3P_2O_8$.	$FePO_4$.	CaF_2.	Quartz.	Total.
84·30	2·03	0·38	6·62	6·35	99·69

The colour appears to be due to the manganese, which exists, for the most part, as manganous phosphate. L. J. S.

"Mangankiesel" from the Harz. By FRIEDRICH KLOCKMANN (*Jahrb. k. Preuss. geol. Landesanst. u. Bergakad.*, 1895 (1894), **15**, p. xxxii).—In a quartz-schist on the Steinbergkappe, in the Western or Upper Harz, is a band, 1 foot thick, of compact, reddish-white to grey "mangankiesel"; analysis by Erbrich gave

MnO.	CaO.	MgO.	CO_2.	SiO_2.	Undeter.	Total.
32·251	0·477	0·910	18·097	49·009	0·756	101·500

This occurrence is very similar to that at Schebenholz, near Elbingerode. L. J. S.

The Genesis of the Talc Deposits of St. Lawrence Co., N.Y. By CHARLES H. SMYTH, jun. (*School of Mines Quart.*, 1896, **17**,

333—341).—In the gneissic area of the Adirondacks are large belts of crystalline limestones which often contain tremolite and enstatite; these minerals sometimes predominate, and the limestones graduate into tremolite and enstatite schists. Intimately associated with these schists, and, in fact, graduating into them, are the talc deposits. The talc, being pseudomorphous after these fibrous minerals, is itself fibrous in structure, this structure being parallel to the cleavage of the original mineral. For a very soft specimen, apparently derived from enstatite, the optic axial angle was determined as 56° 36′, and for a slightly harder piece, 80° 34′; these values are much greater than is usual for talc, and they evidently decrease with the progress of alteration of the original mineral. With this fibrous talc ("agalite") is also a little of the more usual form of foliated talc in soft, pearly scales; this is almost optically uniaxial, and, unlike the former, is not pseudomorphous in origin but of independent growth. The alterations would have been effected by circulating water containing carbonic acid, probably under pressure, as shown by the equations

$$\underset{\text{Enstatite.}}{4MgSiO_3} + H_2O + CO_2 = \underset{\text{Talc.}}{H_2Mg_3Si_4O_{12}} + MgCO_3$$

$$\underset{\text{Tremolite.}}{CaMg_3Si_4O_{12}} + H_2O + CO_2 = \underset{\text{Talc.}}{H_2Mg_3Si_4O_{12}} + CaCO_3.$$

This substitution of H_2 for Ca is in agreement with Clarke's acid metasilicate formula for talc. The resulting carbonates would be carried away by the excess of carbonic acid. These talc deposits have, then, been derived from tremolite and enstatite schists, which, in turn, have originated by the metamorphism of a siliceous magnesium limestone poor in alumina. L. J. S.

Minerals of the Gross-Venediger in the Hohe Tauern. By Ernst Weinschenk (*Zeits. Kryst. Min.*, 1896, **26**, 337—508).—The Gross-Venediger of the Austrian Alps consists of a central mass of granite surrounded by eclogites, amphibolites, gneisses, schists, phyllites, &c., these containing isolated patches of serpentine. The secondary mineral veins occurring in these rocks are of two distinct types. One is of general distribution, and is characterised by the presence of a little titanic acid; the minerals of constant occurrence are quartz, felspar, apatite and calcite, whilst the other minerals depend on the kind of rock containing the veins. The other type of veins occurs in connection with the serpentines, and is of local distribution; here quartz and felspar are absent, and the surrounding rocks have no influence on the mineral contents of the veins.

Detailed descriptions are given of 60 mineral species found in the district, and analyses are given of the following:—I, Pistachio-green epidote, occurring with magnetite and diopside in an epidote-rock in connection with the serpentine. II, Red garnet. III, Massive garnet, from a garnet-chlorite-rock, which is an alteration product of serpentine; the crystals of II rest on this massive garnet, and the two are very similar in appearance, but differ in composition. IV, Hyacinth-red garnet from an epidote-idocrase-rock. V, Clove-brown garnet from a rock containing epidote, diopside and magnetite. VI, Hyacinth-

red garnet. VII, Brown garnet. The above analyses of garnet, with the exception of III, by Muthmann, are quoted from H. Schnerr (*Inaug.-Diss., Munich*, 1894). VIII, Acicular diopside from crevices in a hornblende schist. IX, Light green diopside. X, Albite from crevices in amphibolite and eclogite; it contains also Na_2O, 11·19; K_2O, 0·19 per cent.

	SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	FeO.	MnO.	MgO.	H_2O or loss on ignition.
I.	38·15	23·51	14·32	23·41	0·18	—	—	1·93
II.	36·33	7·35	21·64	32·36	1·91	0·48	—	0·29
III.	38·32	17·38	7·56	31·72	2·49	1·50	0·48	0·71
IV.	37·53	11·99	14·79	33·55	1·68	0·28	—	0·48
V.	35·97	7·07	22·51	31·51	2·88	trace	—	0·25
VI.	37·96	16·29	8·73	31·98	4·46	0·57	—	—
VII.	36·56	7·44	20·94	23·59	1·17	trace	—	—
VIII.	52·08	1·96	—	23·31	9·21	0·35	12·75	—
IX.	54·19	0·07	—	22·76	2·05	0·43	20·24	—
X.	67·76	20·15	—	0·77	—	—	—	—

L. J. S.

Disintegration and Decomposition of Diabase. By GEORGE P. MERRILL (*Bull. Geol. Soc. Amer.*, 1896, 7, 349—362).—The diabase of a large dyke at Medford, Massachusetts, has been extensively disintegrated to a reddish-brown, sandy material. The fresh rock is quite firm, but contains some calcite, a little zeolite and chlorite, and shows a slight kaolinisation of the felspars. Under I, is the bulk analysis of the fresh diabase, and under II, that of the portion soluble in hydrochloric acid and sodium carbonate solution (1·19 per cent. of the silica being soluble in the former). Under III, is that the bulk analysis of the disintegrated rock, and IV, is that of the soluble portion (0·85 per cent. of the silica being here soluble in hydrochloric acid). These analyses show that the disintegration is accompanied by decomposition and a leaching out of the more soluble constituents. As would be expected, more of the fresh rock is soluble in acid and alkaline solutions than of the altered rock. Analysis V, is of the fine silt and clay, which forms only 3·17 per cent. of the altered rock. 78·87 per cent. of it is soluble in hydrochloric acid and sodium carbonate, and under the microscope the material shows felspar and other silicates.

	I	II	III	IV	V	VI	VII
SiO_2	47·28	10·85	44·44	9·50	36·61	8·48	18·03
Al_2O_3	20·22	4·74	23·19	4·86	40·68	0·00	0·00
Fe_2O_3	3·66	10·91	12·70	10·00		2·42	18·10
FeO	8·89						
CaO	7·09	3·09	6·03	1·50	3·44	1·83	25·89
MgO	3·17	2·20	2·82	1·84	4·02	0·68	21·70
MnO	0·77	n.d.	0·52	n.d.	n.d.	0·32	41·57
K_2O	2·16	1·21	1·75	0·68	1·82	0·62	29·15
Na_2O	3·94	0·50	3·93	0·17	2·14	0·50	12·83
P_2O_5	0·68	n.d.	0·70	n.d.	—	0·08	11·39
Ignition	2·73	2·73	3·73	3·73	10·97	0·53	0·00
Total	100·59	36·23	99·81	32·28	99·68	14·93	—

Column VI gives the percentage loss for the entire rock, as calculated from I and III, on the supposition that the total amount of alumina has remained unaffected during the alteration of the rock, and column VII gives the percentage loss of each constituent, as calculated from I and VI. Calculating the results on this basis brings out points which are not obvious on mere inspection of the bulk analyses of the fresh and altered rock ; for example, it is seen that calcium, potassium, iron and magnesium have been relatively largely removed. The analyses of the granite of the district of Columbia (Abstr., 1896, ii., 483) are here recalculated in this manner. The assumption that the total amount of alumina remains constant is taken from Roth, but it does not always seem to be correct, for in some cases ferric oxide is more refractory than the alumina.

The relative rapidity of rock weathering in high and low latitudes is discussed, and it is insisted that the rapid disintegration in warm, moist climates has been emphasised too much. Here, decomposition follows more closely upon disintegration, whilst in cold regions, where the action of frost is a potent factor, disintegration exceeds decomposition. The term degeneration, to include both disintegration and decomposition, is proposed. L. J. S.

Dust which fell [in Austria-Hungary] in February, 1896. By CONRAD H. VON JOHN (*Verh. k.k. geol. Reichsanst.*, 1896, 259—264). —On February 25th. and 26th., 1896, there was a fall of dust and snow over a large area in Hungary, mainly about the Platten See, but extending into Austria as far north as Austrian Silesia. The dust from different localities is very similar, being dark brown, and of extreme fineness. Under the microscope, the principal constituent is seen as grains of a grey, transparent, amorphous material, which analysis shows to be a clay. There are also black particles of organic matter, numerous grains and splinters of quartz, and a few fragments of augite, zircon, rutile, etc. Mica and remains of organisms were not found. The first four of the following analyses are of material from different localities. All contain a little carbonic acid and organic matter. The first contains 2·92 and the second 2·48 per cent. of carbon.

SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	K_2O.	Na_2O.	H_2O (at 100°).	Loss on ignition.	Total.
49·29	15·50	6·17	4·23	2·46	2·94	1·02	2·80	16·09	100·50
52·25	13·95	7·10	3·85	2·45	3·05	1·46	2·78	12·96	99·85
52·50	14·20	6·40	3·80	2·45	2·97	1·44	3·02	13·80	100·58
55·28	15·24	6·58	3·66	2·63	[2·57]		3·01	11·03	100·00
45·10	15·95	13·25	4·85	2·64	1·95	0·85	6·70	8·84	100·47

The great similarity shown in these analyses points to a common origin for the dust. The decrease in silica to the north is explained by quartz having fallen before the other constituents. The last of the above analyses is of Nile mud (containing also 0·34 SO_3, 1 per cent. C, and some CO_2), and it is suggested that the dust in question came from Egypt ; as, however, there was no storm at Alexandria from 21st. to 26th. of February, it may have come from Servia and S. Hungary. L. J. S.

The Arlington Iron. By NEWTON H. WINCHELL (*Amer. Geologist*, 1896, **18**, 267—271).—This iron was found in March, 1894, at $2\frac{1}{2}$ miles north-east of Arlington, Sibley Co., Minnesota. It is roughly heart-shaped, with an average thickness of 1 inch; weight $19\frac{3}{4}$ lbs. The convex side is tolerably smooth and has a spotted appearance, whilst the opposite, nearly plane, surface is pitted and rough, some of the pits almost penetrating the specimen. Three structural directions, brought out by etching, are described in detail. Analysis by F. F. Sharpless gave:

Fe.	Ni.	Co.	P.	Total.
90·781	8·605	1·023	0·045	100·454

Also Cr, Cu, and combined carbon in traces; S, Si, and Mn are absent. The composition does not appear to be uniform, as four determinations of the iron varied between 90·58 and 91·74; the carbon also varies. L. J. S.

Discovery of Argon in the Gases of a Spring at Perchtoldsdorf, near Vienna. By MAX BAMBERGER (*Monatsh.*, 1896, **17**, 604—612). The gas from the same spring was investigated in 1853 by Ragsky, who showed that the gas contains 93·8 per cent. of nitrogen. The author confirms Ragsky's analyses, but, also finds that the gas described as nitrogen by Ragsky contains 1·11—1·24 per cent. of argon. J. J. S.

Water from a Mineral Spring in Mitchell Co., Kansas. By EDGAR H. S. BAILEY and MARY A. RICE (*Trans. Kansas Acad. Sci.*, 1896 (1893—4), **14**, 40—41).—Water from a spring 2 miles east of Cawker City and half a mile south-east of the celebrated "Great Spirit Spring," in Mitchell Co., Kansas, gave in parts per 100,000: SiO_2 and insoluble matter, 1·53; Fe_2O_3 and Al_2O_3, 1·66; CaO, 38·66; MgO, 61·48; SO_3, 269·50; K_2O, 21·20; Na_2O, 753·30; Cl, 740·00; B_2O_3, trace; CO_2 (calculated), 35·69. This composition is very similar to that of the water of the "Great Spirit Spring." L. J. S.

Thermal Spring at Wiesbaden. By C. REMIGIUS FRESENIUS and ERNST HINTZ (*Jahrb. Nassau. Ver.*, 1896, *Jahrg.* **49**, 3—23).—The water of the Augusta Victoria bath at Wiesbaden has a temperature of 40°; sp. gr. = 1·006455 at 14°. Analysis gave, in parts per 1000: NaCl, 6·644452; KCl, 0·172013; LiCl, 0·018825; NH_4Cl 0·012666; $CaCl_2$, 0·599187; NaBr, 0·004920; NaI, 0·000025; $CaSO_4$' 0·068816; $SrSO_4$, 0·024678; $BaSO_4$, 0·001381; $CaH_2(CO_3)_2$, 0·364834, $MgH_2(CO_3)_2$, 0·248852; $FeH_2(CO_3)_2$, 0·001392; $MnH_2(CO_3)_2$, 0·001716; $Ca_2As_2O_7$, 0·000045; $Ca_3P_2O_8$, 0·000081; CaB_2O_4, 0·002565; SiO_2,; 0·059782; free CO_2, 0·282091; total, 8·508321. Also traces of rubidium, cæsium, nitric acid, titanic acid, copper, and organic substances. This composition is very similar to that of other thermal waters of Wiesbaden containing sodium chloride; analyses of these are quoted for comparison. Full analytical details are given in the paper. L. J. S.

Carbonated Water from Seifersdorf (Austrian Silesia). By ERNST LUDWIG (*Tsch. Min. Mitth.*, 1896, **16**, 133—139).—Water from a spring at the village of Seifersdorf, in Austrian Silesia, gave, in 10,000 parts: K_2SO_4, 0·057; Na_2SO_4, 0·037; NaCl, 0·058; Na_2CO_3, 1·775; $CaCO_3$, 7·171; $SrCO_3$, 0·021; $MgCO_3$, 1·000; $FeCO_3$, 0·179; $MnCO_3$, 0·026; Al_2O_3, 0·001; SiO_2, 0·620; organic matter, 0·040; CO_2 in bicarbonates, 4·499; CO_2 free, 17·449; total solids, 10·985; also traces of lithium and phosphoric acid. Sp. gr. = 1·00163 at 17·2° (compared with distilled water at the same temperature). The composition of the water remains constant throughout the course of the year, and the temperature only varies from 10—12°. The rocks of the district are limestones, clayey sandstones, and also some of volcanic origin. L. J. S.

The Constantin-Spring in Gleichenberg (Styria). By ERNST LUDWIG (*Tsch. Min. Mitth.*, 1896, **16**, 140—149).—The celebrated mineral waters of Gleichenberg, Styria, were known to the Romans; analyses of the water of the Constantin-spring have previously been made by Schrötter (1834) and Gottlieb (1864). The results of the present analysis are, in parts per 10,000: K_2SO_4, 1·023; KCl, 0·012; NaCl, 18·223; $Na_2B_4O_7$, 0·082; Na_2HPO_4, 0·006; Na_2CO_3, 25·060; Li_2CO_3, 0·039; $CaCO_3$, 3·541; $SrCO_3$, 0·054; $BaCO_3$, 0·004; $MgCO_3$, 4·215; $FeCO_3$, 0·027; $MnCO_3$, 0·002; Al_2O_3, 0·002; SiO_2, 0·647; organic matter, 0·054; CO_2 in bicarbonates, 14·212; CO_2 free, 20·519; total solids, 52·937; also traces of cæsium and rubidium. These results agree, in the important constituents, with the older analyses, so that there has been no change in the composition of the water during the last 60 years. Sp. gr. = 1·0057 at 17·6° (compared with distilled water at the same temperature). The temperature of the water is 17·3°. The rocks of the district are mainly trachytes, together with basalts and Tertiary sands and marls. From the water, opal has been deposited in the trachyte, and pebbles and plants have been cemented together by a siliceous deposit. L. J. S.

Deposit from a Chalybeate Water. By E. C. CASE (*Trans. Kansas Acad. Sci.*, 1896 (1893—4), **14**, 36—37).—Water from a well near Lawrence, and close to the bank of the Kansas River, gave, in parts per 100,000: SiO_2 and insoluble matter, 4·50; Fe_2O_3 and Al_2O_3, 3·45; $CaSO_4$, 9·31; $CaCO_3$, 15·03; $MgCO_3$, 6·72; NaCl, 14·43; total solids, 53·44; CO_2 (free and in bicarbonates), 25·01. The water is at first clear, but, on standing, soon becomes turbid. In the well is a homogeneous deposit having the following composition, which approaches that of limonite: SiO_2 and insoluble matter, 19·30; Fe_2O_3 with a little Al_2O_3, 46·95; H_2O below 100°, 9·15; H_2O at 230°, 14·40; $CaSO_4$, 0·25; $CaCO_3$, 7·32; $MgCO_3$, 0·75; NaCl, 0·60 per cent.; organic matter, not determined. From this it is seen that the silica has remained in solution to a larger extent than the iron. The well is sunk in gravel containing nodules of limonite, and this has been dissolved by the percolating carbonated water; the iron in the freshly-drawn water exists in the ferrous state. L. J. S.

Physiological Chemistry.

Absorption of Dextrose in the Small Intestine, and the Effects of Drugs on the Process. By FRIEDRICH VON SCANZONI (*Zeit. Biol.*, 1896, **33**, 462—474).—Ethereal oils, oil of mustard, alcohol, pepper, and orexin have, in certain concentrations, a favour able influence on the absorption of dextrose in the intestine, as in the stomach. In the stomach, the absorption may be increased fivefold, but this is not nearly so well marked in the intestine; the rise is only a few degrees per cent., for the intestine is already, in normal circumstances, the ideal place for dextrose absorption. The dose necessary to stimulate the intestine is smaller; for instance, oil of mustard (1 in 200) has no harmful effect on the stomach and stimulates the absorption process there, but it is harmful to the intestine.

W. D. H.

Absorption of Peptone in the Small Intestine, and the Effect of Drugs on the Process. By ERNST FARNSTEINER (*Zeit. Biol.*, 1896, **33**, 475—488).—A 1 per cent. aqueous solution of peptone was introduced through a fistula into the ileum in a dog, and after 15 minutes, 63 per cent., on the average, was absorbed.

Addition of 5 per cent. alcohol raised this figure to 72—74; oil of mustard (1 : 1500—5000) to 72—73; oil of cinnamon (1 : 500) to 69. The effect of these drugs is not so marked as in the stomach. Bitters like quassia have no constant action. Mucilages hinder absorption; 2 per cent. of starch brings the absorption down to 21—25 per cent.

W. D. H.

Changes in Cane Sugar in the Alimentary Canal. By HEINRICH KÜBNER (*Zeit. Biol*, 1896, **33**, 404—407).—Inversion of cane sugar does not occur in the stomach, nor in artificial gastric digestion. The statement often made to the contrary is owing (1) to dextrose being present from the remains of the previous meal; (2) to the ingestion of sugar which had previously been partly inverted; and (3) to the fact that in pathological cases, especially if there is a transudation of serum into the stomach, inversion may occur.

Inversion begins in the small intestine; cane sugar is, however, resistant, and may be found in small amounts quite low down the intestine. Absorption of cane sugar occurs most rapidly in the stomach and duodenum.

W. D. H.

Iron in the Animal Organism. By WINFIELD S. HALL (*Chem. Centr.*, 1896, i, 970; from Du Bois Reymond's *Archiv*, 1896, 49—83).—Carniferrin was added to food free from iron, and given to white mice; the tissues being examined microchemically by the ammonium sulphide method, and control experiments made on mice that had had no carniferrin. The whole animals were also incinerated, and the iron estimated in the ash. In those fed only on food free from iron, there was

a loss of 40 per cent. in the total iron of the body in three weeks. In those fed on carniferrin, the red corpuscles increased in number, and absorption of the iron was found to occur chiefly in the duodenum, and to a less extent in the jejunum. Storage of iron occurred in the spleen, and to a less extent in the liver. The liver, large intestine, and kidney appear also to excrete iron. W. D. H.

The Value of Rhamnose in the Normal and Diabetic Organism. By LUDWIG LINDEMANN and RICHARD MAY (*Chem. Centr.*, 1896, i, 932—933 from *Deutsch. Arch. Klin. Med.*, **56**, 283—294).—In a healthy man, about 8 per cent. of the rhamnose given was recovered in the urine; in a diabetic patient, 11·7 per cent. in the urine and 4·4 per cent. in the fæces was recovered; there was a simultaneous excretion of dextrose, but the nitrogenous output was diminished from 17 to 14·8 grams per diem. Rhamnose acts, therefore, as a proteid-sparing food. W. D. H.

The Proteids of Leucæmic Urine. By RUDOLF KOLISCH and RICHARD BURIÁN (*Chem. Centr.*, 1896, i, 972—973, from *Zeits. Klin. Med.*, **29**, 374—380).—Albumosuria is not a constant feature in leucæmia; when present, it probably originates from the decomposition of leucocytes, the increase in alloxuric substances in the urine supporting this view. The principal new point made out in the case described is the occurrence of Lilienfeld's histon in the urine.
W. D. H.

Luciferase, or the Light-producing Enzyme of Animals and Plants. By RAPHAEL DUBOIS (*Compt. Rend.*, 1896, **123**, 653—654).—The author is of opinion that the active agent in the production of light by certain animals and plants is a substance having the general characters of an enzyme, to which he therefore gives the name *luciferase*, and that it is not the result of slow oxidation. The luminiferous organs of the glow-worm, and the eggs contained in the ovaries of the female, give with tincture of guaiacum, a fine, blue coloration, as does also the luminous mucus from the surface of dead fish after treatment with chloroform water and filtration. A. C. C.

Analyses of Human, Cows', and Mares' Milk. By WILLIAM CAMERER and FRIEDRICH SÖLDNER (*Zeit. Biol.*, 1896, **33**, 535—568. Compare Abstr., 1896, ii, 378).—A very large number of analyses of human, cows', and mares' milk are given; in the case of human milk, the different dates of lactation are stated. The paper is chiefly composed of tables of results, which cannot be conveniently shortened, and do not appear to show any new points of interest.
W. D. H.

Constancy of the Freezing Points of Milk and other Organic Liquids. By J. WINTER (*Bull. Soc. Chem.*, 1896, [3], **15**, 162—163).—The author finds that his observations (Abstr., 1896, ii, 199) have been to some extent anticipated by Beckmann.

Excretion of Calcium in Diabetes. By Ernst Tenbaum (*Zeit. Biol.*, 1896, **33**, 379—403).—The increased amount, both of liquid and solid nutriment taken by diabetics, accounts, in large measure, for the increase in the volume of urine and amount of nitrogen excreted. When such increase occurs, the quantity of calcium salts in the urine increases also in a proportionate way. The large output of calcium appears to be dependent solely on the increased nutriment taken. Calcium and proteid are so closely associated that this is what would be expected. W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

The Changes which take place in Milk, either Spontaneously, or during Culinary Processes. By ANTOINE BÉCHAMP (*Bull. Soc. Chim.*, 1896, [3], 15, 96).—An historical sketch of the development of the germ theory of fermentation of organic solutions. M. W. T.

Putrefaction of Albumin. By OSKAR EMMERLING (*Ber.*, 1896, **29**, 2721—2726).—In these experiments, pure proteids were treated with pure cultivations of micro-organisms.

I. Behaviour of wheat gluten with *Proteus vulgaris*. Wheat paste freed from starch by treatment with malt and repeated washing with water, and from fatty substances by washing with alcohol and ether, was mixed with calcium carbonate, potassium phosphate, and magnesium sulphate, and placed in the Koch steam steriliser for 3 days, it was then mixed with the *Proteus* and kept in an incubator at 37°; after 4 days, gas began to be evolved, which consisted of 46 per cent. CO_2, 38 per cent. H, and 16 per cent. N. After 14 days, the process was stopped, and the strongly alkaline liquid distilled in a current of steam. *The distillate* consisted of phenols and volatile bases, from which trimethylamine was isolated and identified. *The residue* contained the non-volatile bases, and the acids as their calcium salts; in the former, betaine was present, and was isolated by means of its aurochloride (m. p. 227°). The acids were separated by the fractional precipitation of their silver salts, formic, acetic, and butyric acids being identified.

II. Behaviour of Egg albumin with *Staphylococcus pyogenes aureus*. The decomposition products, isolated in the same way, were found to be, in *the distillate*, phenol, indole, and scatole, and in *the residue, volatile*, formic, acetic, propionic, butyric, and traces of higher fatty acids; *non-volatile*, oxalic and succinic acids. Betaine and trimethylamine were also present. J. F. T.

A New Bacillus which forms Butyric Acid from Glycerol. By OSKAR EMMERLING (*Ber.*, 1896, **29**, 2726—2727).—This bacillus, for which the author proposes the name *Bacillus boocopricus*, is isolated from cow-excrement by Fritz's method. It is very similar to *B. subtilis*, and grows well on gelatin. With beef broth, it does not form indole. With glycerol, at 36°, in the presence of calcium

carbonate, methylic alcohol, acetic acid, butyric acid, and traces of formic and succinic acids are produced; 6 grams of alcohol, 4·5 grams of acetic acid, and 7 grams of normal butyric acid being obtained from 600 grams of glycerol. From grape sugar, ethylic alcohol and lactic acid are produced. J. F. T.

The Cause of Poisoning by Curtains containing Arsenic. By OSKAR EMMERLING (*Ber.*, 1896, **29**, 2728).—As the result of a large number of experiments conducted with different bacilli and micrococci, the author states that in no case is hydrogen arsenide evolved from fabrics containing arsenic by their means. It is, therefore, highly improbable that poisoning from woollen stuffs containing arsenic is due to hydrogen arsenide, evolved by the action of a micro-organism.

J. F. T.

Denitrifying Bacteria and the Loss of Nitrogen caused by them. By R. BURRI and ALBERT STUTZER (*Ann Agron.*, 1896, **22**, 491—494; from *Centr. Bact. Par.*, 1895, 1, 2 Abt., 257, 350, 392 and 422).—From horse-dung, two bacteria were isolated, which together, but not singly, decomposed nitrites with liberation of free nitrogen. The one was identified as *Bacterium coli commune*, whilst the other is new, and is designated *B. denitrificans I.* Another variety, *B. denitrificans II.*, which alone liberates nitrogen from nitrates and nitrites, was isolated from old straw. This micro-organism throve in artificial solutions as well as in nitrate-broth, and destroyed the nitrate in the same length of time. *B. coli* with *B. denit. I.*, however, caused no turbidity in the artificial solution in a week, and did not decompose the nitrate in the least, in absence of complex nitrogen compounds.

The destruction of nitrates (in both) is checked when the amount of nitrate present exceeds 0·5—0·6 per cent. This holds both for *B. coli* with *B. denit. I.* and for *B. denit. II.* This has nothing to do with the production of nitrite (which is not poisonous, as the author formerly supposed), but to excessive alkalinity.

In the presence of 0·06—0·07 per cent. of phosphoric acid the fermentation produced by *B. coli* with *B. denit. I.* was checked, whilst *B. denit. II.* remained active in presence of 0·14 per cent. of phosphoric acid.

Quantitative experiments with *B. denit. II.* in artificial solutions, showed that 22·2, 20·3 and 20·6 per cent. of the nitrogen of the nitrates remains, and is probably in the form of proteids. On one occasion, 79·5, on another 82·7, per cent. was evolved as gas. Neither carbonic anhydride nor nitrous oxide could be detected.

In the complete absence of oxygen, *B. denit. I.* with *B. coli* reduce nitrates completely, but without evolution of nitrogen, the nitrate being almost entirely converted into nitrite. With very limited access of air, *B. denit. I.* will develop sufficiently to give rise (in conjunction with *B. coli*) to evolution of free nitrogen; whilst with abundant aëration the evolution of nitrogen is normal.

B. denit. II. decomposes nitrates normally in complete absence of air, whilst with aëration, the fermentation is hindered or completely stopped. N. H. J. M.

Origin of Trimethylamine, and the Spontaneous Development of Heat in Hops. By JOHANNES BEHRENS (*Bied. Centr.*, 1896, **25**, 713—714; from *Der Bierbrauer*, 1896, 578—579).—Whilst, according to Griesmayer and Greshoff, trimethylamine is a constituent of hops, the author was unable to detect its presence either in fresh hops, or in hops which had been kept in the dry state. In presence of water, however, hops acquire a very repulsive odour, in which that of trimethylamine can readily be detected. This change, and the rise of temperature which accompanies it, is due to a bacterium (*Bacillus lupuliperda*) which resembles Flügge's *B. fluorescens putibus* both morphologically and physiologically. The nitrogenous substances of the hops which are utilised by the bacillus are proteids, choline, ammonia, and asparagine, whilst malic and citric acids, &c., supply carbon. The tannin present in the hops does not seem to be changed by the bacillus. The antiseptic nature of hops prevents the development of other micro-organisms. N. H. J. M.

Action of Phenylquinolines and Phosphines on Lower Organisms. By A. J. F. HERMANN TAPPEINER (*Chem. Centr.*, 1896, i, 1010—1011; from *Deutsch. Arch. Klin. Med.*, **56**, 369—380).—Those organisms (Infusoria, Amœbæ, Turbellaridæ) on which quinine works strongly are even more readily killed by phenylquinolines and phosphines; those (yeasts, bacteria) on which quinine has but little action are less affected by the compounds in question. Of the phenylquinolines, the β-compound acts most strongly, the α-compound least so.

W. D. H.

Vegetation in Respired Air. By LOUIS MANGIN (*Bied. Centr.*, 1896, **25**, 689—690; from *Jour. Agric. prat.*, 1896, i, 491—493).—Equal quantities of seeds and tubers were placed, with equal amounts of water, in each of a series of receivers through which air was drawn by means of a pump. The apparatus was so constructed that a small quantity of air could be withdrawn for analysis. As the air became richer in carbonic anhydride and poorer in oxygen, growth was considerably retarded. Whilst linseed absorbed 3·29 per cent. of oxygen, and produced 1·44 per cent. of carbonic anhydride in an atmosphere containing 1 to 3 per cent. of carbonic anhydride, the amounts were 1·45 and 1·04 per cent. when 2 to 5 per cent. of carbonic anhydride was present. In the case of peas, the amount of substance produced diminished from 53·5 to 42·5 grams when the percentage of carbonic anhydride rose from 1—3 to 2—5 per cent. There was, moreover, a change in the nature of the oxidation process indicated by an increase in the quotients CO_2/O_2. With linseed, for instance, this was 0·51 in an atmosphere containing 1—3 per cent. of carbonic anhydride, and 0·74 when the percentage was 2—5 N. H. J. M.

Production of Vegetable Proteids. By TAMÁS KOSUTÁNY (*Landw.-Versuchs.-Stat.*, 1896, **48**, 13—32). The object of the author's experiments was to throw light on the question whether assimilation, and the process of reduction which it involves, influences the production of proteids from asparagine. Assuming that amides are formed

from proteids as secondary products of oxidation in germinating seeds, it seemed likely that, in developed plants, proteids might be formed from amides in the process of deoxidation under the influence of light.

Comparative experiments were made in which the one half of a number of leaves of *Riparia sauvage* were cut during the day (between 2 and 3 p.m.), the remaining halves being separated from the plants in the night, and analysed.

The percentage of total nitrogen diminished as the season advanced. In the 1894 experiments, the difference was about 0·25 per cent. (from 21st June to the end of August), but in 1895, with a longer interval, the percentage diminished from 5·314 (on May 8) to 1·25 at the end of October. As regards variations in composition during day and night, the total nitrogen was somewhat higher during the night than in the day time (102·37 : 100), but the non-proteid nitrogen is much less by night than by day (45 : 100). The leaves contain rather more ammonia but less nitric acid in the night than in the day time. Since, in the night, oxidation prevails in the plant, it is probable that the conversion of nitrates into proteids is greatest in the night. No asparagine, or similar substance, could be detected in the leaves cut off in the night. It is concluded that, whilst the crude substances which produce proteids are chiefly taken up by the plant in the day time, their actual conversion into proteids takes place more in the night than in the day.

The leaves contain on the average 1·10 per cent. more water in the night than in the day time. Leaves cut in the day time contain the most sugar, those cut in the night the most free acids.

The percentage of ash increased, somewhat irregularly, from 9·43 on May 8 to 19·93 on October 23. N. H. J. M.

Effect of Nitrogen on Root Formation. By HERMANN MÜLLER (*Bied. Centr.*, 1896, **25**, 595—597; from *Jahresber. Versuchs-stat. Wädensweil.*, 1895, **4**, 48).—Water-culture experiments were made in which half of the roots of a number of plants were immersed in nutritive solutions free from nitrogen, the other half in solutions containing nitrogen. The plants selected were vetches, maize, sunflower, and beans, &c. In presence of nitrogen, the root-development was greatly increased. It is concluded that proteids are formed in the roots, and not in the leaves only; otherwise, it must be assumed that the proteids migrated to the roots directly supplied with nitrogen, and not to those (of the same plants) growing in solutions free from nitrogen. N. H. J. M.

The Physiological Significance of Lecithin in Plants. By JULIUS STOKLASA (*Ber.*, 1896, **29**, 2761—2771).—The important part which is played by phosphoric acid in plant physiology has led the author to determine the proportion of lecithin occurring in certain vegetable organs; the paper forms a summary of the analytical results and the conclusions which they suggest. Seeds which are rich in albumin contain also a greater proportion of lecithin, whilst oily seeds, those, for instance, of *Brassica oleracea, Sinapis arvensis*, and *Beta vulgaris*, are poor in lecithin; germination of the last-named is not accompanied by decomposition of lecithin, but in the case of *Pisum*

sativum this process involves reduction in the percentage of the substance in question. In the fruit of maize, 74 per cent. of the total quantity of lecithin is found in the embryo and scutellum, only 26 per cent. occurring in the endosperm; from this fact, the author concludes that the lecithin in the scutellum, and especially in the embryo, under the influence of radiant energy, serves to elaborate chlorophyll in the early stages of plant life. Development of the leaf is also associated with the production of lecithin, which increases with the multiplication of chlorophyll granules; this increase is in some way related to the assimilation of carbonic anhydride, and it appears probable to the author that lecithin arises in the granules themselves as a product of assimilation. Moreover, analyses show that vine leaves, when allowed to grow for 10 days in darkness, contain only one-third as much lecithin as similar, but unprotected, leaves from the same plant collected at the same time of day (4 o'clock).

*Chlorolecithin** is an amorphous, greenish-black substance with metallic lustre, which has been isolated from freshly-gathered, unpressed grass leaves; its behaviour towards baryta indicates the presence of choline, glycerylphosphoric acid, and chlorophyllan groups, and, in this respect, it resembles Hoppe-Seyler's chlorophyllan, differing from that substance, however, in the amount of phosphorus present, for whilst chlorophyllan contains only 1·38 per cent., chlorolecithin contains 3·37 per cent.

Thus the author has traced an intimate connection between lecithin and chlorophyll, and maintains that, not only does the former substance actually occur in chlorophyll granules, but that phosphorus is a constituent of chlorophyll, and that without this element the elaboration of chlorophyll and the development of chlorophyll granules is impossible.

Examination of apple-blossom has shown that the pedicel is engaged in transmitting lecithin from the leaf to the flower. The petals are richest in lecithin previous to fertilisation, acting as storage vessels, which become rapidly depleted of lecithin when the fruit is formed. The pollen contains 6 per cent. of lecithin, and, Zacharias having shown that nucleïn occurs in this product, it is noteworthy that animal spermatozoa also contain lecithin and nucleïn. M. O. F.

Coexistence of Laccase and Tyrosinase in certain Fungi. By GABRIEL BERTRAND (*Compt. rend.*, 1896, **123**, 463—465).—An extract of various species of *Russula* obtained by plasmolysis with washed chloroform or ether, has much more active oxidising properties than extracts prepared by the methods previously described. It also acts on tyrosin, in addition to having the oxidising properties of laccase, and it would seem that both ferments are present in the extract. This is confirmed by the fact that, when the extract is heated at 70°, the power of affecting tyrosin disappears, whilst the extract still attacks the substances that are oxidised by laccase. When an extract of *Russula delica* in aqueous chloroform is mixed with excess of alcohol, a precipitate is formed, and the liquid does not attack tyrosin, but oxidises phenols and amines in the same manner as laccase. The precipitate, when purified by suspension in chloroform and reprecipitation by alcohol, yields

* This is not a chlorinated derivative of lecithin, as its name would seem to imply —[EDITORS].

an aqueous solution which has practically no action on phenols and amines, but rapidly oxidises tyrosin. It follows that laccase and tyrosinase coexist in the juice of many species of fungi (compare Abstr., 1896, ii, 61, 268, 571). C. H. B.

Nitrogenous Constituents of Beet-Juice. By EDMUND O. VON LIPPMANN (*Ber.*, 1896, **29**, 2645—2654).—Of the nitrogenous compounds present in beet-juice, the following have been already obtained and more or less carefully characterised: asparagine, glutamine, betaïne and choline, leucine and tyrosine, glutamic or pyroglutamic acid, citrazinic acid, lecithin, and legumin.

The author has already pointed out (Abstr., 1888, and *Zeit. f. Rubenzuck. Ind.*, **38**, 68) that, besides lecithin, the cell-substance contains other phosphorus compounds, which may be extracted by means of alkalis, and are probably closely related to the nucleïns, and, further, that their decomposition products, the xanthine-compounds, may be obtained from the molasses by fractional precipitation with phosphotungstic acid. He has now succeeded in isolating a considerable number of nitrogenous substances in the following manner.

The dilute solution of the decomposition products was neutralised and precipitated with lead acetate, phosphotungstic acid, or mercuric nitrate, and the precipitates formed were then decomposed, in order to liberate the contained bases, which were subsequently fractionally precipitated by means of phosphotungstic acid, mercuric nitrate, mercuric chloride, &c.

The following substances were isolated and completely characterised: xanthine, guanine, hypoxanthine, adenine, carnine (rarely observed in plants), arginine, guanidine, allantoïn, and possibly vicin. The investigation is complicated by the occurrence of the decomposition products of these substances.

The recurrence of vicin, a glucoside, in the above product of alkaline hydrolysis is not impossible, as would at first sight appear, as Drenkmann has described a glucoside (*Zeit. f. Rubenzuck. Ind.*, **46**, 478) which is only slowly decomposed by strong alkali at high temperatures.

A. L.

The Maximum of Plant Production. By ADOLF MAYER (*Landw. Versuchs.-Stat.*, 1896, **48**, 61—76).—The maximum production of the various agricultural plants, as grown in ordinary agricultural practice, was previously shown (*ibid.*, 1892, **40**, 205) to be 7000—8000 kilos. per hectare in Northern Europe, although by very heavy manuring twice that amount, or more, could be obtained.

With regard to the question whether the limit of production depends on the amount of sunlight or on the amount of carbonic anhydride in the air, the results of Dehérain's experiments on sugar beet (Abstr., 1890, 406), in which a greater yield was obtained under the influence of farmyard manure, as compared with minerals, seem to point to the production of carbonic anhydride from the organic manure as the cause of the increased yield, especially as the soil to which minerals were applied was shown to be poor in carbonic anhydride. (Dehérain attributed the greater yield on the dung-plot to the direct assimilation of organic matter.) In 1893 and 1894, the author made experiments with sugar beet (on plots of 0·25 are) in which plants received (1) farmyard manure

(120,000 kilograms per hectare), (2) minerals, and (3) minerals in conjunction with carbonic anhydride (liberated on the spot from 10 per cent. dextrose solution and yeast). The results indicated that the highest yield of sugar beet can be obtained with exclusively mineral manure, when sufficiently watered, as well as with farmyard manure. It is not possible to explain Dehérain's results, as the plan of the experiments is not fully given; but it seems likely that the beneficial effect of the farmyard manure must, at any rate, be largely due to the increased water-capacity of the soil. N. H. J. M.

Nutritive Value of Horse-chestnuts. By PAUL GAY (*Ann. Agron.*, 1896, **22**, 401—423).—The horse-chestnuts employed in the experiments had the following percentage composition.

Water.	Crude proteïn.	Ether extract.	N-free extract.	Crude cellulose.	Ash.
38·93	4·81	4·64	46·19	3 66	1·77

Two lots of sheep were fed with lucerne (500 grams), peas (500 grams), with the addition of mangolds and horse-chestnuts respectively, given in such quantity that the amount of dry matter of each was the same. The increase of live weight was much greater in the case of the sheep fed with chestnuts than with those fed with roots. On reversing the foods, the same result was again obtained. It is concluded that raw chestnuts are about three times as nutritive as mangolds. The value of chestnuts is considerably increased by cooking. In experiments with cows, in which 5 kilos. of chestnuts per head per day were given, it was found that no effect was produced either on the taste or composition of the milk, and the milk had no injurious effect on calves. The yield of milk was, however, considerably diminished (from 15 to 12 kilos. per day). This is ascribed to deficiency of water in the food, in which case the remedy would be easy.

Pigs declined to eat chestnuts in any quantity, and left more than half the food with which they were mixed. N. H. J. M.

Molasses as Food for Cows. By AUGUST STELLWAAG (*Bied. Centr.*, 1896, **25**, 718—719; from *Zeit. landw. Ver. Bayern*, 1895, 778). —Four cows were fed for a week with chaff (two-thirds hay and one-third straw, 20 kilos.), fresh brewers' grains (20 kilos.), malt germs (2 kilos.), and crushed barley (4 kilos. per 1000 kilos. live weight). For two of the cows, the same feeding was continued four weeks longer; whilst the other two, instead of the barley, had molasses mixed with an equal weight of palm cake (3 kilos.). During the next four weeks, the food of the two sets of cows was reversed. The composition of the molasses food resembled that of the barley, but contained somewhat less carbohydrates and rather more fat. The cows consumed the whole of the molasses mixture (which was mixed with the brewers' grains), and did not suffer from indigestion. There was no change, either in the amount of milk or in the percentage of fat, during the experiments.

N. H. J. M.

Recent Progress in Soil Examination. By EUGENE W. HILGARD (*Rep. Agric. Exper. Stat. Univ. Cal. for* 1894—5, 23—32).—A number of Californian and Hawaiian soils were analysed, employing Dyer's

citric acid extraction method, and the results obtained agreed exceedingly well with vegetation experiments.

With regard to the recognition of "nitrogen hunger" in soils, the author recommends separation and analysis of the humus. The more nitrogenous the humus is, the less carbon will be oxidised by the limited amount of oxygen present in the soil. It was previously concluded that a soil in which the humus contained less than 2·5 per cent. of nitrogen would be benefited by nitrogenous manure, notwithstanding that the soil itself contained as much as 0·17 per cent. of nitrogen. This opinion was confirmed by a vegetation experiment, which clearly showed that available nitrogen was deficient. The amount of lime present in the soil is, however, of great importance in this connection. With a deficiency of lime, soils would show "nitrogen hunger," even when the humus contained more than 2·5 per cent. of nitrogen, whilst in calcareous soil, a low percentage of nitrogen might suffice.

The author thinks that the examination of humus, in conjunction with Dyer's method for mineral constituents, will eventually furnish a means of readily ascertaining the wants of soils, although the vegetation tests (in pots or in the field) will have the last word. N. H. J. M.

Behaviour of Superphosphate and Basic Slag in Soil. By St. Smorawski and H. Jacobson (*Bied. Centr.*, 1896, **25**, 580—581; from *Blätter f. Zuckerrübenbau*, 1896, **3**, 193—201).—Basic slag and mineral and bone superphosphates respectively (about 1 per cent.) were mixed with soil, and the phosphoric acid soluble in water and in citrate solution was determined. The soil was then put into beakers, moistened with water, and left to dry, being occasionally stirred. The phosphoric acid was again determined as before. This was repeated several times at intervals of 4 to 8 weeks.

The results indicate that the phosphoric acid originally soluble in water is very rapidly converted into the citrate-soluble form, but this has no effect on its value as manure. The citrate-soluble phosphate seems to undergo no further change. The alleged inferiority of basic slag is, therefore, unfounded.

Mineral and bone superphosphates containing the same percentage of phosphoric acid have equal value as manures. N. H. J. M.

Assimilability of Nitric and Ammoniacal Nitrogen by Plants. By Aimé Pagnoul (*Ann. Agron.*, 1896, **22**, 485—490).—Mangolds, *Camelina*, clover, and oats were grown in sterilised sand, (1) without any manure, (2) with sodium phosphate and potassium nitrate, and (3) with sodium phosphate, potassium chloride, and ammonium sulphate; as compared with nitrate, ammonium sulphate gave two or three times as much dry produce in each case. The unmanured plants were quite free from nitrates. The plants which received nitrate contained 0·35 to 0·75 per cent. of nitrogen as nitrates (in the dry substance), whilst those which received ammonium sulphate contained much less, but still quite appreciable amounts (0·017 to 0·150 per cent.). Nitrogen in the form of ammonia was found in the plants manured both with nitrate and with ammonium sulphate, but in much smaller quantity than nitric nitrogen. The results indicate that, under the

conditions of the experiments, nitrogen was directly assimilated in the form of ammonia, and in greater quantity than in the form of nitrates.

Nitrogen as nitrates was determined in the plants as follows: After drying the substance at 105°, a small quantity (0·2 gram) was boiled with a little water, and, when cold, treated with a few drops of lead acetate solution, and about a gram of animal charcoal. After an hour, it was filtered and diluted to 50 c.c.; of this solution, 5 c.c. was evaporated to dryness, well stirred with a few drops of phenol dissolved in sulphuric acid (1 : 7), and treated with ammonia. The yellow colour thus produced, if nitrates were present, was compared with that of a standard solution of ammonium picrate (N = 1 per million), by pouring the two solutions into two similar tubes, each holding 50 c.c. and divided into c.c. The solution to be tested is diluted until it has the same tint as 50 c.c. of the standard solution, and its volume V (in c.c.) read. The amount of nitrogen in milligrams per cent. =

$$\frac{V \cdot 10000}{2000} = 5V.$$

Ammonia was determined by distilling the fresh substance (10 grams) with water (50 c.c.), magnesia (0·5 gram), paraffin (0·5 gram), and a few pieces of pumice, using a spiral condenser; the distillate, which is collected in a flask containing a few drops of very dilute sulphuric acid, is diluted to 50 c.c. and treated with Nessler solution, employing, for comparison, a solution of ammonium sulphate (N = 1 per million). N. H. J. M.

The Agricultural Value of Deteriorated Phosphatic Manures. By JULES JOFFRE (*Bull. Soc. Chim.*, 1896, [3], **15**, 42—46).—Millot has proved that the deterioration of phosphatic manures is due to the formation of an insoluble ferric phosphate. To determine the relative values of superphosphate, tricalcium phosphate, and the ferric phosphate obtained from a sample of manure containing very little tricalcium phosphate, from which all the soluble phosphate had been removed, crops of mustard were grown in plots which differed only with regard to the nature of the phosphate present.

The results were as follows.

Plot without fertiliser	100
Plot with ferric phosphate from deteriorated superphosphate	167
Plot with tricalcium phosphate	280
Plot with superphosphate	360

M. W. T.

Analytical Chemistry.

Methods of Rock Analysis. By MAX DITTRICH (*Mitth. Badisch. geol. Landesanst.*, 1894, 3, 75—105).—The methods are essentially those usually adopted, the material being first fused with sodium and potassium carbonates; several small variations are described in detail.

L. J. S.

Estimation of the Three Halogens, Chlorine, Bromine, and Iodine, in Mixtures of their Binary Compounds. By A. A. BENNETT and L. A. PLACEWAY (*J. Amer. Chem. Soc.*, 1896, **18**, 688—692). —Two grams of the mixed salts is dissolved in 150 c.c. of water; 50 c.c. of a 20 per cent. solution of iron alum is added, and the iodine is expelled by distillation; this, as usual, is condensed in an apparatus containing 35 c.c. of 20 per cent. potassium iodide and titrated.

The bromine is then liberated by adding 35 c.c. of a saturated solution of potassium permanganate and distilling, in the usual way, into potassium iodide solution, when it sets free an equivalent quantity of iodine.

After reducing the excess of permanganate with sulphuric acid and ferrous sulphate, the chlorine is precipitated with silver nitrate.

L. DE K.

Action of Bromine on Metallic Chlorides and a Method for the Estimation of both Halogens in the presence of one another. By FRITZ BLAU (*Monatsh.*, 1896, **17**, 547—566).—The author has taken the experimental numbers obtained by Berthelot (Abstr., 1881, 342; 1883, 8; 1885, 632) in his experiments on the amount of chlorine liberated by the action of bromine on different chlorides, and from these has calculated the affinity constant K by means of the equation $K^2 = \frac{(A-C)\,(B-C)}{C^2}$ where A = the number of equivalents of chloride originally present, B = those of bromine, and C = the (necessarily equal) number of equivalents of bromide and chlorine produced in the reaction. The results thus obtained are roughly of the same magnitude, and differ completely from those based on Humpidge's data (Abstr., 1884, 1245). This divergence can probably be accounted for by the inaptitude of the indirect method for the estimation of chlorine and bromine when one of these is present in a large excess. The author has carried out experiments on the action of bromine on concentrated sodium chloride solutions. In making the experiments, a measured quantity of a solution of pure sodium chloride was placed in a stoppered flask, and a weighed quantity of pure bromine, contained in a small, thin-walled bulb, dropped in; on shaking, the bulb was broken, and the flask was placed in the dark at a constant temperature for several hours. The excess of bromine and the liberated chlorine were then quickly removed by a rapid current of air which had been filtered through cotton wool, and as soon as the last trace of bromine was thus removed, the amounts of sodium bromide and chloride in the solution were estimated. Exact analytical results were obtained by using a modification of Berglund's method (Abstr., 1885, 836) for the estimation of bromide and chloride in the presence of one another. For this purpose, the bromine was set free by means of potassium permanganate and potassium hydrogen sulphate; and the solution distilled in a vacuum at the ordinary temperature in a special apparatus, the bromine being collected in aqueous potash. The hypobromite thus formed was converted into bromide, and the liquid treated exactly as before, the bromine in the second distillate being estimated by means of iodine. The residues in the two distillation flasks were united, and the amount of chloride contained in them estimated.

The author finds that at 12—13° $K = 272 \cdot 67$, and at 16—17° $K = 246 \cdot 08$.

Care was taken to show that no secondary actions took place, as the solution formed was quite neutral. It was also proved experimentally that the current of air always removed the two halogens in the same proportion, so that the equilibrium was not disturbed.

J. J. S.

Jacobsen and Brunn's Method for the Purification by means of Iodine of Hydrogen Sulphide containing Arsenic. By ZDENKO H. SKRAUP (*Chem. Centr.*, 1896, i, 469; from *Zeit. Österr. Apoth.-V.* **34**, 72—76).—In testing the efficiency of this method (Jacobsen, Abstr., 1887, 885), which is based on the facts that hydrogen arsenide and dry iodine form arsenic tri-iodide, whilst hydrogen sulphide and iodine do not react in the absence of water, the gas, after washing with water and subsequent drying by means of calcium chloride, was passed over dry iodine, then into sodium hydroxide solution (?) and then into warm nitric acid. The residue obtained on evaporating the nitric acid was treated with sulphuric acid and submitted to Marsh's test. Slow passage of the gas through the apparatus was found to effect either a complete removal of arsenic or to leave only slight traces, but unsatisfactory results were obtained when a more rapid current was employed.

E. W. W.

Estimation of Sulphur in Pyrites. By GEORG LUNGE (*J. Amer. Chem. Soc.*, 1896, **18**, 685—686).—A final reply to Gladding (Abstr., 1895, ii, 291, and 1896, ii, 622). Experiments conducted on behalf of the author have again shown that, when precipitating a sulphate with barium chloride solution, the latter may be added either quickly and in moderate excess, or run in from a burette at the rate of one drop per second without any sensible difference in the result.

L. DE K.

Estimation of Sulphides in Calcium Carbide. By FREDERICK J. POPE (*J. Amer. Chem. Soc.*, 1896, **18**, 740—741).—A weighed quantity of the sample is introduced into a dry Erlenmeyer flask provided with a stop-cock funnel and a delivery tube leading to a 10 oz. wash-bottle, which is in turn connected with a smaller one; both are partially filled with a standard solution of lead acetate, the total value of which is, of course, accurately known. The calcium carbide is first decomposed by water until no more acetylene is evolved, and excess of dilute sulphuric acid is then introduced and the mixture boiled; hydrogen sulphide is evolved, and precipitates part of the lead as sulphide. The excess of lead is then estimated by the author's method (this vol., ii, 125).

L. DE K.

Estimation of Sulphur in Ores. By J. H. STANSBIE (*Chem. News*, 1896, **74**, 189). LUCIEN L. DE KONINCK (*ibid.*, 224).—Stansbie suggests the use of nitric acid and bromine for the oxidation of sulphur in ores, whilst de Koninck points to a similar application of the same reagents by himself years ago.

D. A. L.

Estimation of Sulphuric Acid or of Barium. By JAMES EDMUNDS (*Chem. News*, 1896, **74**, 187—188).—For the proposed method, there

are required decinormal and centinormal solutions of barium nitrate, potassium chromate, silver nitrate, sodium chloride, and potassium sulphate, centinormal solutions of potassium thiocyanate and calcium sulphate, and a decinormal solution of ferric sulphate. The latter is made by oxidising a solution of ferrous sulphate by boiling with nitric acid, then boiling with a large excess of sulphuric acid to expel the nitric acid, and making up to the strength of a decinormal solution of iron in about a quinquenormal sulphuric acid. The calcium and potassium sulphate solutions serve for tests and controls. In use, 10 c.c. of the decinormal solutions of barium nitrate, potassium chromate, and silver nitrate are added successively to 70 c.c. of the liquid under examination, contained in a tall 200 c.c. stoppered bottle, shaking vigorously for one minute after each addition. The mixture is preferably allowed to subside, or may be filtered, and 20 c.c. of the clear liquid is mixed with a measured excess of decinormal sodium chloride, and titrated back with centinormal silver nitrate, using potassium chromate as indicator. From the data obtained, the content of sulphuric acid is calculated. The liquid tested should have the strength of a centinormal solution; if stronger, it should be diluted, if weaker, concentrated, or the centinormal reagents employed throughout. Moreover, as a preliminary, substances precipitating barium or chromates, or reducing the latter, also ammonia, &c., must be eliminated, and any haloids present must be estimated, for which purpose the thiocyanate and ferric sulphate are provided. In estimating barium, the 70 c.c. of liquid under examination being of suitable strength, is first shaken with 10 c.c. of decinormal potassium sulphate, then the excess of sulphuric acid is estimated in the above manner.

D. A. L.

[Estimation of Nitric and Ammoniacal Nitrogen in Plants.] By AIMÉ PAGNOUL (*Ann. Agr.*, 1896, **22**, 485—490).—See this vol., ii, 120.

Wet Method for Estimating Carbon and Nitrogen in Organic Compounds. By PAUL FRITSCH (*Annalen*, 1896, **294**, 79—88).—The derivatives of isoquinoline described by the author (Abstr., 1895, i, 624) were analysed by a new method, which combines Messinger's process for estimating carbon (Abstr., 1889, 80; 1890, 1467) with Krüger's modification of Kjeldahl's method for determining nitrogen (Abstr., 1894, ii, 258).

The substance to be analysed is oxidised by means of potassium dichromate and concentrated sulphuric acid in a small distilling flask through which a current of purified air is passing. The gas produced is then passed into a heated combustion tube 36 cm. in length, containing a mixture of granulated copper oxide and lead chromate between two copper spirals. After being dried with calcium chloride, the carbonic anhydride is absorbed by potash. The residue in the flask is transferred to a larger distilling flask, connected with a Liebig's condenser, and the ammonia liberated on treatment with caustic soda is determined in the ordinary manner.

Figures illustrate the form of apparatus employed, and analytical details are described in the paper.

M. O. F.

Analysis of Mortars. By WILLIAM J. DIBDIN and ROBERT GRIMWOOD (*Analyst*, 1896, **21**, 197—204).—The authors have analysed a large number of limestones, bricks, and mortars, and have tabulated the results.

In estimating lime and sandy matter in mortars, it must be remembered that, in practice, the mortars are made by volume and not by weight. The best plan, therefore, is to prepare a mortar according to the particular specification and to analyse this side by side with the inspected sample, allowing, of course, for difference in moisture, &c. The authors also give convenient factors for reducing the weights to volumes.

Earthy matter is estimated by treating the sample with dilute hydrochloric acid and repeatedly decanting from the heavy sandy matter; the earthy matter is then filtered, dried, and weighed. The filtrate contains the soluble silica, calcium, &c., which are then estimated as usual. From the amount of the former, a very fair idea as to the quantity of added cement may be obtained. L. DE K.

Colorimetric Estimation of Lead. By MAURICE LUCAS (*Bull. Soc. Chim.*, 1896, [3], **15**, 39—42).—The author describes a method for estimating very small quantities of lead in alloys, &c. The lead and copper are separated by electrolysis, using a current of 0·3 ampère and 2 volts.; the lead, which is deposited on the positive pole in the form of peroxide, is, after washing, drying, and weighing, redissolved in 1 c.c. of the nitric acid containing nitrous acid, obtained by the electrolysis of nitric acid. The solution is rendered neutral with caustic soda and diluted so that 50 c.c. of water contains about 1 milligram of lead; five drops of ammonium sulphide is now added, and the colour of the liquid compared with that of solutions containing the same quantity of sodium nitrate and ammonium sulphide, to which different quantities of a standard solution of lead nitrate have been added.

Sodium carbonate and neutral salts have a considerable effect on the colour of the lead sulphide, consequently great care must be taken to keep the conditions exactly the same in the different solutions.

M. W. T.

Volumetric Estimation of Lead. By FREDERICK J. POPE (*J. Amer. Chem. Soc.*, 1896, **18**, 737—740).—The lead should be in the form of acetate. Lead sulphide (galena) is first converted into sulphate by the action of mixed nitric and sulphuric acids, and after removing the free acid, it is dissolved in ammonium acetate; the lead is now precipitated by adding an excess of standard solution of potassium dichromate, and the lead chromate is filtered off. The excess of chromate is then estimated by adding an excess of standard arsenious acid solution and a little dilute sulphuric acid, stirring until the yellow colour has completely disappeared or changed to a faint green; after adding a slight excess of sodium hydrogen carbonate, the excess of arsenious acid is titrated with standard solution of iodine. The calculation will be easily understood. The test analyses are remarkably accurate. L. DE K.

Estimation of Iron and Aluminium Oxides in Phosphate Rock. By THOMAS S. GLADDING (*J. Amer. Chem. Soc.*, 1896, **18**,

717--721; 721—724).—Four grams of the finely-ground sample is heated for half-an-hour with 30 c.c. of dilute hydrochloric acid (1—1). This will leave any iron pyrites undissolved. After filtering, the iron is fully oxidised with nitric acid, and the liquid made up to a definite bulk.

An aliquot part of the solution, representing, say, one gram, is neutralised with ammonia and well cooled; more ammonia is then added until a permanent precipitate has formed, and this is again dissolved by cautiously adding hydrochloric acid. 15 c.c. of ammonium acetate (made by neutralising 30 per cent. acetic acid with ammonia) and 5 c.c. of acetic acid are placed in a beaker, and the phosphate solution is slowly added, with constant stirring. After keeping it at 60° for about an hour, the precipitate is collected and washed with a 10 per cent. ammonium acetate solution, redissolved in a few c.c. of hot hydrochloric acid (1—4), and one gram of ammonium phosphate is added. Ammonia is added until the liquid is turbid, then hydrochloric acid until the precipitate just redissolves, and the liquid is again poured into 15 c.c. of ammonium acetate and 5 c.c. of acetic acid. The precipitate formed is treated again in the same way, when a product is obtained free from calcium and consisting of normal aluminium phosphate with normal iron phosphate. The two are weighed together, and the iron phosphate is estimated volumetrically.

In another method, the solution is made as detailed above, but instead of using ammonium acetate, it is run into a solution of potassium hydroxide (500 grams per litre), and heated at 70° for about an hour. From the filtrate, the aluminium is recovered by first adding ammonium phosphate, then hydrochloric acid in slight excess, and precipitating the aluminium phosphate from this solution by means of acid ammonium acetate in the way already described. The iron may be estimated in the precipitate produced by the potash. L. DE K.

Estimation of the Iron in Blood for Clinical Purposes. By ADOLF JOLLES (*Montash.*, 1896, **17**, 677—696).—The first method described is as follows. A suitable quantity of the blood is evaporated to dryness, the residue strongly ignited, and then dissolved by fusing it with perfectly anhydrous potassium hydrogen sulphate, about 1 gram of the latter being used for each c.c. of blood originally taken; the operation is best conducted in a platinum crucible, but one of good Berlin porcelain may be used. The contents of the crucible are then rinsed with hot water into a beaker, poured into a flask, treated with dilute sulphuric acid and pure zinc (the amount of iron in which has been previously estimated; about 1 gram of zinc is used for every 1—2 c.c. of blood taken), boiled until all the zinc has dissolved (the flask being closed with a Bunsen valve), and the amount of iron finally titrated with N/50 or N/100 permanganate. In 10 samples of the blood of one and the same pig, the amount of iron found, per 1,000 grams of the blood, varied from 0·662 to 0·687; in the blood of eight different pigs, it varied between 0·549 and 0·948.

A second method is to evaporate the strongly ignited residue from 3—5 grams of the blood several times with strong hydrochloric acid

on the water bath, dissolve the residue in water, and precipitate in the cold with a solution of nitroso-β-naphthol (1—2 grams of the pure crystallised substance in 100 c.c. of 50 per cent. acetic acid), using about 5 c.c. of the solution per 3 grams of blood taken. The very bulky precipitate is collected, washed with small quantities of 50 per cent. acetic acid, dried at 100° and finally ignited, the residual ferric oxide being weighed. The whole operation requires about 45 minutes, and the results agree well with those obtained by the first method.

A third colorimetric method is recommended for clinical purposes. It requires two similar Nessler cylinders, graduated up to 15 c.c., and furnished with taps near the bottom; also a ferric solution, for purposes of comparison, made by fusing 0·0358 grams of pure ferric oxide with 50 grams of anhydrous potassium hydrogen sulphate, dissolving the product in water and making up to 500 c.c. 0·05 c.c. of blood is measured in a capillary pipette, rinsed out into a crucible, and evaporated to dryness; the residue is strongly ignited and fused with 0·1 gram of potassium hydrogen sulphate, and the cooled mass is rinsed with hot water into one of the cylinders and diluted to the 10 c.c. mark, whilst in the other cylinder 1 c.c. of the ferric solution is placed, and diluted to 10 c.c. To each cylinder is then added 1 c.c. of dilute hydrochloric acid (1 : 3), and 4 c.c. of ammonium thiocyanate solution (7·5 grams per litre), and the liquid is run out from the more deeply-coloured solution until the tint is seen to be the same on looking down through the two solutions. In this way, the amount of iron in the blood can be calculated, the specific gravity of the blood being also determined, if required, by Hammerschlag's method (*Zeitschr. klin. Med.*, **20**, 244), which requires only a single drop of blood. The percentage amount varied, in 10 adult men, between 0·526 and 0·720; in one anæmic man, it was only 0·441, and in an anæmic woman, 0·433. The results by this method agree well with those obtained by the other two methods, and 10—15 minutes suffice for making the experiment. C. F. B.

Volumetric Estimation of Molybdenum and of Vanadium. By CARL FRIEDHEIM (*Ber.*, 1896, **29**, 2981—2985).—Mainly a reply to Gooch and Fairbanks's criticisms (this vol., ii, 76), on the method previously described by the author and Euler (Abstr., 1895, ii, 535). The author shows that as good results can be obtained by his simpler method (*loc. cit.*) as by Gooch and Fairbanks's more complex one, provided the mixture is not heated too rapidly, so that no hydrogen iodide may be evolved before the air in the flask has become replaced by iodine vapour. The heating need only be continued until the liquid becomes clear green; further heating, as recommended by Gooch and Fairbanks, is useless. J. J. S.

Solubility of Bismuth Sulphide in Sodium Sulphide; Estimation of Small Amounts of Bismuth in Anti-Friction Alloys. By THOMAS B. STILLMAN (*J. Amer. Chem. Soc.*, 1896, **18**, 683—684).—The author has found that bismuth sulphide is sensibly soluble in solution of sodium sulphide (sp. gr. 1·06) at the boiling temperature. If, when analysing an alloy containing but a few per cent. of bismuth, the neutralised solution is boiled as usual with

75 c.c. of the sodium sulphide, the loss in bismuth will be very great, whilst fractions of a per cent. may escape detection altogether.

L. DE K.

Estimation of Ethylene in the Presence of Benzene Vapour. By FRITZ HABER and H. OECHELHÄUSER (*Ber.*, 1896, **29**, 2700—2705). —Ethylene is completely absorbed by bromine water, as Treadwell and Stokes have stated, although this is denied by Winkler. Benzene, too, is almost entirely removed by this treatment, but in a purely mechanical manner; no chemical action takes place, for bromine vapour mixed with benzene vapour can be exposed to diffused light for 2 minutes without any loss of bromine occurring. It is thus possible to estimate the amount of ethylene by absorbing with a measured quantity of bromine water of known strength, and determining the residual bromine; this was done by treating the bromine water, while still in the burette, with potassium iodide, and subsequently titrating with thiosulphate. The bromine water was sucked into the (Bunte) burette through the lower tap, and its volume measured in the burette itself, the volume between the lowest graduation and the stop-cock having been previously determined. In this way, the Carlsruhe coal-gas was found to contain 3·85 per cent. of ethylene; the contraction, after treatment with bromine water and the addition of potassium iodide, was 4·4 per cent.; the difference is, of course, benzene.

C. F. B.

Limiting the Explosive Proportions of Acetylene and Detecting and Measuring the Gas in the Air. By FRANK CLOWES (*Chem. News*, 1896, **74**, 188).—The author's determinations show that the limits of explosiveness of mixtures of acetylene and air are reached with 3 and 82 per cent. of the former gas; from 22 per cent. upwards, the burning is accompanied by the separation of carbon. The corresponding limits for hydrogen are 5 and 72, for methane, 5 and 13. Even in quantities far below the explosive limit, acetylene tinges the author's standard hydrogen flame a yellowish green, and gives a well-defined, pale bluish "cap," which with a hydrogen flame 10 mm. high, attains a height of 17, 19, 28, and 48 mm. for 0·25, 0·5, 1, and 2 per cent. of acetylene respectively, whereas 2·5 and 2·75 per cent. of that gas give caps 56 and 79 mm., in height over a 5 mm. hydrogen flame.

D. A. L.

General and Physical Chemistry.

Stereo-chemical Spectrometric Researches, I. By JULIUS W. BRÜHL (*Zeit. physikal. Chem.*, 1896, **21**, 385—413; *Ber.*, 1896, **29**, 2902—2913).—The author has determined the molecular refraction and dispersion in the case of a number of stereoisomeric compounds. In the case of those compounds which could not be examined in the liquid state, solutions were prepared, and it was observed that, in order to obtain the best results, the solvent should have a refraction and dispersion as nearly as possible equal to those of the compound itself.* The compounds examined were: (I) monobromo-ψ-butylene, dimethylacetylene hydrobromide; α-tolane dichloride, β-tolane dichloride; *syn*-anisaldoxime, *anti*-anisaldoxime; α-benzilmonoxime, β-benzilmonoxime; α-nitroformaldehyde-hydrazone, β-nitroformaldehyde-hydrazone; and (II) cinnamic acid, allocinnamic acid, cinnamylideneacetic acid, allocinnamylideneacetic acid; methylic cinnamate, methylic allocinnamate, ethylic cinnamate, ethylic allocinnamate; *anti*- and *syn*-metadibromodiazobenzene cyanide. The compounds may be divided into two classes, as indicated, in the first of which the refraction and dispersion are equal, or nearly so, the differences being usually within the experimental errors; these compounds include haloids, oximes, and hydrazones. In the second class, which includes acids, ethereal salts, and diazo-compounds, the values of the spectro-constants do not agree, and in this heterospectric class, it is noteworthy that, in every case, the higher melting, less soluble compound has the greater refraction and dispersion. In all cases, the observed numbers are considerably higher than the values calculated from the chemical composition; this is probably due to the elevating influence of the ethylene-phenyl unions. Similar results had been obtained by Walden (Abstr., 1896, ii, 633) in the case of the fumarates and maleates, but the author considers that further research is necessary before deciding whether the differences in the heterospectric compounds are due to a real difference of constitution. L. M. J.

Changes of Rotation in the Passage from Acid to Lactone. By W. ALBERDA VAN EKENSTEIN, W. P. JORISSEN, and L. THEODORUS REICHER (*Zeit physikal. Chem.*, 1896, **21**, 383—384).—The rotations of a number of acids and of the corresponding lactones were determined, and the numbers obtained are given in the accompanying table, the values for the molecular rotation being divided by 10^3.

* This was observed by Perkin to obtain also in the case of the magnetic rotation. (Trans., 1896, 1056.)

Acid.	Mol. rotation of Ion.	Mol. rotation of Lactone.	Diff.
Ribonic	+0·2°	−3·0°	3·2°
Gluconic (*d*)	+1·3° to +1·8°	+11° to 12·1°	10·8° to 9·2°
Mannonic (*d* and *l*)	+2·0°	−9·5° to −9·8°	11·7°
Saccharinic	−1·1°	+15·2°	16·3°
Isosaccharinic	−1·1°	+10·2°	11·3°
Saccharic	+2·6°	+7·3° to 8·0°	9·9° to 10·6°
Mannosaccharic	+0·2°	+35·1°−35·6°	35·2°
α-Rhamnohexonic	+1·3°	+16·3°	15·0°
α-Glucoheptonic	+1·6°	−11·2°	12·8°
Gulonic (*d* and *l*)	±2·7°	∓9·9°	12·6°

L. M. J.

Spectrum of Chlorophyll. By Alexandre L. Étard (*Compt. rend.*, 1896, **123**, 824—828).—Knowledge of chlorophyll can only be extended by examination of large quantities of a chlorophyll of definite chemical composition. As a matter of fact, chlorophylls are comparatively stable compounds, and can be treated with ordinary reagents for the purpose of elucidating their chemical structure. In spectroscopic examinations, it is essential that the chlorophyll be a definite chemical species, dissolved in definite proportion in a given solvent, and examined in a layer of definite thickness.

The author gives drawings of the spectra of α-medicagophyll, $C_{28}H_{45}NO_4$, dissolved in carbon bisulphide and in alcohol of 90°, and of α-borragophyll, $C_{34}H_{53}NO_{12}$, in the same solvents, the concentrations in each case being 1 : 400, 1 : 1000, 1 : 10000.

Mere variations in the thickness or concentration of the solution examined are sufficient to cause one chlorophyll to be taken for another. In solutions of 1 : 10000, only the principal orange band remains visible. In carbon bisulphide, the bands are displaced towards the red as compared with the alcoholic solution, but they are particularly well-defined. The spectra of medicagophyll from lucerne and borragophyll from borage are distinctly different in the number and position of the bands; the former shows three bands between the general absorption at the red and violet ends, the latter five. C. H. B.

Chemical Action of the Röntgen Rays. By Alexander von Hemptinne (*Zeit. physikal. Chem.*, 1896, **21**, 493—496).—The electric conductivities of a number of salt solutions were determined, and no alteration was found to occur when the solutions were placed in the path of the Röntgen rays. In the case of solutions sensitive to light, such as silver nitrate in alcohol, and mercuric chloride with ammonium oxalate, the results obtained were doubtful, the effect, if any, of the rays being extremely small. The radiation was also found to have no effect on the velocity of hydrolysis of ethylic acetate, from which the author concludes that the Röntgen rays do not influence ionisation. A mixture of hydrogen and chlorine was not affected, and negative results were like-

wise obtained with a mixture of chlorine and carbonic oxide, so that their chemical activity appears to be very slight. L. M. J.

Action of Metals and their Salts on Röntgen Rays. By JOHN H. GLADSTONE and WALTER HIBBERT (*Chem. News*, 1896, **74**, 235).—The authors find that all metals transmit the Röntgen rays more or less, lithium being almost absolutely transparent, gold practically opaque, and there is every gradation between these two extremes; the order of absorption of the rays is that of the atomic weights, but the absorption increases more rapidly than the atomic weights. Metallic salts show absorption analogous to that of the metal; in fact, the absorption of a dry salt is the sum of the absorptions of its constituents. In solutions, the absorption seems to be that of the salt itself plus that of the solvent.
D. A. L.

Irreversible Cells. By A. E. TAYLOR (*J. Physical Chem.*, 1896, **1**, 1—20 and 81—90).—The author has continued the work of Bancroft (Abstr., 1894, ii, 4) on single-liquid polarisable cells, with especial reference to the effect of the negative ion on the potential difference between an electrode and the electrolyte in which it is immersed. The results confirm Bancroft's conclusion that, with mercury as one pole of the combination, the influence of the negative ion of the salt solution is appreciable, but concentration has no effect on the electromotive force of the cell. It has been shown by Gouy and others, on measuring single potential differences by means of the change of the surface tension of mercury, that an error might be introduced in some cases where there was the possibility of the formation of complex mercury salts. If dropping mercury electrodes do not always give correct results, the solution pressure of a metal is independent of the nature of the negative ion. In every case where the electromotive force of a cell appears to vary with the negative ion, the possibility of complex salts is present. The author concludes that the potential difference between a metal and an electrolyte is not a function of the negative ion of the salt solution, and that in certain cases dropping mercury electrodes do not give correct values for the single potential differences measured by that method. H. C.

Hexamethylenetetramine Salts. By MARCEL DELÉPINE (*Compt. rend.*, 1896, **123**, 888—891).—The author has determined the heats of saturation of hexamethylenetetramine by hydrochloric, sulphuric, nitric, and acetic acids, and the heats of dissolution of the hydrochloride, of the three sulphates, and of the two nitrates.

For the heats of saturation (1 mol. each of acid and base in 1 litre), the following numbers are given.

	Cal.		Cal.
$\frac{1}{2}$HCl	1·13	$\frac{1}{2}HNO_3$	1·15
HCl	2·13	HNO_3	2·19
2HCl	2·32	$2HNO_3$	2·37
$\frac{1}{4}H_2SO_4$	2·11	$\frac{1}{2}C_2H_4O_2$	0·53
$\frac{1}{2}H_2SO_4$	3·51	$C_2H_4O_2$	0·81
H_2SO_4	4·10	$2C_2H_4O_2$	1·06

The addition of the second half equivalent of acid, therefore, produces less heat than the first. The results point to the slight dissocia-

tion of the neutral salt in solution. The following heats of dissolution of the base and its crystallised salts are given.

$C_6H_{12}N_4$ cryst.	$+4{\cdot}80$ Cal.	$C_6H_{12}N_4,HNO_3$	$-5{\cdot}5$ Cal.
$C_6H_{12}N_4,HCl$	$-3{\cdot}94$ "	$C_6H_{12}N_4,2HNO_3$	$-14{\cdot}26$ "
$C_6H_{12}N_4,H_2SO_4$	$-1{\cdot}60$ "	$C_6H_{12}N_4,H_2SO_4+H_2O$	$-4{\cdot}71$ "

from which the following heats of formation are calculated,

$C_6H_{12}N_4$	solid +	HNO_3 solid	$= C_6H_{12}N_4,HNO_3$ solid	$+19{\cdot}09$	Cal.
$C_6H_{12}N_4$	"	$+2HNO_3$ "	$= C_6H_{12}N_4,2HNO_3$ "	$+34{\cdot}63$	"
$C_6H_{12}N_4$	"	$+\frac{1}{2}H_2SO_4$ "	$= C_6H_{12}N_4,\frac{1}{2}H_2SO_4$	$+16{\cdot}09$	"
$C_6H_{12}N_4$	"	$+ H_2SO_4$ "	$= C_6H_{12}N_4,H_2SO_4$	$+26{\cdot}11$	"
$C_6H_{12}N_4,H_2SO_4$	"	$+ H_2O$ liquid	$= C_6H_{12}N_4,H_2SO_4,H_2O$	$+3{\cdot}11$	"
$C_6H_{12}N_4$	"	$+$ HCl gas	$= C_6H_{12}N_4,HCl$ solid	$+28{\cdot}17$	"

The hydrochloride, nitrate, and sulphate are about equally stable in solution, the acetate apparently being more dissociated.

A. C. C.

Heat of Formation of Selenic Acid and Selenates. By RENÉ METZNER (*Compt. rend.*, 1896, **123**, 998—1000).—The heat of neutralisation of selenic acid by sodium hydroxide was found to be $+31{\cdot}19$ Cal., whilst the action of selenic acid on the normal selenate absorbs $-0{\cdot}70$ Cal. Thomsen found $+30{\cdot}39$ Cal. and $-0{\cdot}86$ Cal. respectively, and the corresponding numbers obtained by the author with potassium hydroxide were $+31{\cdot}31$ Cal. and $-1{\cdot}24$ Cal. The heat of neutralisation of the acid by barium oxide is $+36{\cdot}92$ Cal., by lead oxide, $+19{\cdot}81$ Cal.; and by silver oxide, $+18{\cdot}35$ Cal., these values being obtained by double decomposition.

The hydrate, $SeO_3,2H_2O$, was obtained by concentrating the acid under atmospheric pressure at a temperature below 210°, and purifying the first crystals by melting and recrystallisation; the monhydrate, H_2SeO_4, was prepared in a similar way, but the evaporation was in a vacuum. The calorimetric measurements gave the following results.

H_2SeO_4	sol. $+ Aq = SeO_3$	diss. develops	$+13{\cdot}35$	Cal.
H_2SeO_4	liq. $+ Aq = SeO_3$ "	"	$+16{\cdot}80$	"
$SeO_3,2H_2O$	sol. $+ Aq = SeO_3$ "	"	$+7{\cdot}45$	"
$SeO_3,2H_2O$	liq. $+ Aq = SeO_3$ "	"	$+12{\cdot}02$	"

hence the heat of fusion of H_2SeO_4 is $-3{\cdot}45$ Cal., and of $SeO_2,2H_2O$, $-4{\cdot}75$ Cal. and H_2SeO_4 sol. and H_2O sol. $= SeO_3,2H_2O$ sol. develops $+4{\cdot}55$ Cal.

Combining these results with Thomsen's determinations, it follows that

$$\left\{\begin{array}{llll} SeO_2\text{ sol.} + O + H_2O & = H_2SeO_4\text{ diss. develops} & + & 19{\cdot}86\text{ Cal.} \\ SeO_2\text{ ,, } + O + H_2O & = H_2SeO_4\text{ liq. ,,} & + & 3{\cdot}06\text{ ,,} \end{array}\right.$$

$$\left\{\begin{array}{llll} Se + O_3 + H_2O & = H_2SeO_4\text{ diss. ,,} & + & 76{\cdot}66\text{ ,,} \\ Se + O_3 + H_2O & = H_2SeO_4\text{ liq. ,,} & + & 59{\cdot}86\text{ ,,} \end{array}\right.$$

$$\left\{\begin{array}{llll} Se + O_4 + H_2 & = H_2SeO_4\text{ diss. ,,} & + & 145{\cdot}66\text{ ,,} \\ Se + O_4 + H_2 & = H_2SeO_4\text{ liq. ,,} & + & 128{\cdot}86\text{ ,,} \end{array}\right.$$

All the values, except those for hydration, are lower than the corresponding values for sulphuric acid.

C. H. B.

Cryoscopic Researches. By KARL AUWERS and K. ORTON (*Zeit. physikal. Chem.*, 1896, **21**, 337—377).—In order to further attest the

validity of the rules deduced by Auwers (Abstr., 1896, ii, 293), the authors have determined the cryoscopic behaviour of a large number of substituted phenols and also of oxyazo-compounds. The first set of experiments was on the effect of ortho-substituents on various para-phenolic compounds. The aldehyde-group has the most powerful "abnormalising" influence; the cyanogen and methylic carboxy-groups are nearly alike in their effects. Nitro-groups have the strongest "normalising" effect, whilst of the halogens, iodine has the most marked influence. The cryoscopic behaviour of the orthohydroxyazo-compounds leads the authors to the conclusion that these compounds are not phenols, but hydrazones of orthoquinone. The researches were then extended to the derivatives of benzoic acid, but here the influence of the substituent is less marked, as almost all the compounds examined are abnormal, the variations from normal value increasing with the concentration. L. M. J.

Abnormal Freezing Point Depressions. By GUIDO BODLÄNDER (*Zeit. physikal. Chem.*, 1896, **21**, 378—382).—In the experiments made by Ciamician and Garelli on the formation of solid solutions in the case of anthracene and salicylic acid in benzoic acid, the concentration of the salicylic acid in the solid solution was compared with that in the *original* solution, whereas the author points out that comparison should have been made with the solution with which the crystals were in equilibrium; on making this correction, he finds that the ratio is not constant, but varies from 0·68 to 1·08. Similarly, in the experiments with benzene, phenol, and benzil, the ratio of the concentration of the phenol in the solid and liquid solutions varies from 0·309 to 0·198, increasing with dilution. If the molecular weight in the solid phase is calculated from these numbers, it is found to be smaller than that in the liquid, and on the assumption that the solid contains simple molecules, and the liquid simple and double molecules, the author calculates the dissociation of the latter; the results appear to be in accordance with the laws of mass action, but the author does not consider that this must necessarily be the true explanation of them.

L. M. J.

Compressibility of certain Gases at 0° and under nearly Atmospheric Pressure. By ANATOLE LEDUC (*Compt. rend.*, 1896, **123**, 743—745).—The author has determined the compressibility of five gases at pressures ranging from 35 cm. to 113 cm. of mercury, adopting Mariotte's method. The apparatus consisted of a manometer similar to that used by Regnault in the determination of the expansion of gases at constant pressure, with the addition, however, of a third tube, by means of which mercury could be admitted at will without introducing air bubbles. The gas was cooled by immersing the apparatus in a bath of ice-cold water, the temperature of which was accurately observed. Owing to the slight variations of pressure, the author substitutes $A(P - P_0)$ for ϵ in Regnault's expression,

$$\epsilon = \frac{P_0 V_0}{PV} - 1,$$

representing the departure of a gas from Mariotte's law. Expressing

the pressure in centimetres, and taking $P_0 = 76$, the following values of the coefficient A are given.

Carbonic anhydride. $A = 102 \cdot 10^{-6}$, a number which is higher than that obtained by Regnault.

Nitrous oxide. $A = 11 \cdot 10^{-5}$ (approx.).

Hydrogen chloride. At 0°, $A = 120 \cdot 10^{-6}$ (between 76 cm. and 120 cm.).

At 15°, $A = 107 \cdot 10^{-6}$ (between 76 cm. and 120 cm.).

Ammonia. At 0°, $A = 243 \cdot 10^{-6}$ (between 76 cm. and 130 cm.).

At 14°, $A = 190 \cdot 10^{-6}$.

Sulphurous anhydride. $A = 323 \cdot 10^{-6}$.

The following coefficients of expansion of gaseous ammonia between 0° and 14° are given.

Const. press. of 115 cm.	0·00404
Const. press. of 76 cm.	0·00389

A. C. C.

Potential Energy and Virial of Molecular Forces. By G. Bakker (*Zeit. physikal. Chem.*, 1896, **21**, 497—506).—By consideration of the potential energy in a liquid, the author deduces that the ratio between the heat of vaporisation and the difference between the liquid and gaseous densities is proportional to the square of the diameter of the molecules, and hence, under certain conditions, the latter may be compared. L. M. J.

New Method of Determining the Specific Gravity of Liquids. By Roman Zaloziecki (*Zeit. angw. Chem.*, 1896, 552—556). —The principle of the method has already been taken advantage of by Boyle and by Babinet to compare the specific gravities of two different liquids. The author's apparatus consists essentially of a long U-tube, one of the arms of which is calibrated, whilst a stop-cock, a little above the bend, separates it from the bend and the other arm. If the sp. gr. of an aqueous solution is required, the uncalibrated limb is filled with a liquid of low sp. gr., and immiscible with water, such as light petroleum, which answers very well. The aqueous liquid is run into the calibrated tube to a fixed height, and, by opening the tap, the two liquids are brought into contact. The apparatus is plunged for some time in water at 15°, and the difference in the height of the two columns is then recorded in mm. For instance, if the column of aqueous liquid measures 502 mm. (= 500 mm. + 2 mm. allowance for effect of capillarity in a tube 5 mm. broad), its sp. gr. is found by multiplying the difference by 2, adding 1000, and multiplying this by the sp. gr. of the light petroleum. The apparatus may, of course, be used for petroleum, oils, &c.; in this case, water is used in the uncalibrated limb instead of light petroleum. L. de K.

Solution and Fusion. By Wilder D. Bancroft (*J. Physical Chem.*, 1896, **1**, 137—148).—The author discusses the question whether solubility and fusion curves are always identical, or ever so. It is evident that solubility curves cannot in all cases be fusion curves, as the temperature of the experiment is above the fusion temperature of either of the components in many cases. Even where this is not the case, the

author holds that there is a distinction between a fusion curve and a solubility curve. The approximation formulæ for the change of concentration with the temperature have the same form for both curves except that the heat of fusion enters into one, and the heat of dissolution into the other. Since these two quantities are not identical, it follows that there is a radical distinction between the two curves. The partial pressure of the solvent is always less than its vapour pressure as a pure liquid at the same temperature; it is therefore possible for the vapour pressure of the dissolved substance (solute) to be greater or less than its vapour pressure in the pure state, depending on conditions with which we are not yet familiar. Even when two liquids are miscible in all proportions (consolute), it appears that each may still have a definite solubility one in the other. H. C.

Some Abnormal Cases of Solubility. By HENRI L. LE CHATELIER (*Compt. rend.*, 1896, **123**, 746—749).—When certain metallic sulphates are added in increasing quantities to sodium sulphate, the curve representing the melting points of the various mixtures is different in character from those plotted by the author for the mixtures of salts previously examined (comp. Abstr., 1894, ii, 272, 307). In the case of the sulphates of calcium and magnesium, the following numerical results are given, 875° being the melting point of sodium sulphate.

$Na_2SO_4 + CaSO_4$—

Concentration ...	0	1	3	5	7·5	10	20	30	40
Temperature	875°	884°	900°	912°	923°	930°	941°	938°	923°
	46	51	54	57	67	75	100		
	912°	905°	925°	950°	1040°	1130°	(1350°).		

$Na_2SO_4 + MgSO_4$—

Concentration ...	0	5	15	30	35	42	48	50	55
Temperature	875°	870°	830°	740°	690°	655°	675°	700°	730°
	67	70	75	80	100.				
	800°	795°	870°	925°	1170°.				

The effect of the addition, therefore, of the first small proportion of these two sulphates is either to raise the melting point of the mixture, or at least to produce no appreciable lowering. It is probable that this abnormal behaviour is due to the isomorphism of sodium sulphate with the double sulphates formed. When certain fused mixtures of the above sulphates are allowed to solidify, the mass remains transparent even to the point of complete solidification, owing to the formation of crystals which are all of the same nature. The curves representing the melting points of mixtures of sodium sulphate with increasing proportions of the sulphates of calcium, barium, lead, magnesium, and cadmium consist of three parts, the first corresponding with the formation of isomorphous crystals containing the two constituents in varying proportions, the second to the formation of definite double sulphates, and the third to the crystallisation of the added sulphate itself.

A. C. C.

Precipitation of Salts. By H. A. BATHRICK (*J. Physical Chem.*, 1896, 1, 157—169).—Bancroft has shown that the solubility of salts in alcohol can be represented by an equation of the form $(x + A)\ y^n = C$, where x and y denote respectively the quantities of alcohol and of salt

in a constant quantity of water. The author finds by direct experiment that this equation holds for the solubilities of salts in aqueous alcohol and in acetone. The factor n is apparently independent of the temperature. The term A is a function of the salt, the solvent, and the temperature. If x is expressed in reacting weights, the product of A into the reacting weight is independent of the nature of the substance denoted by x. H. C.

The Neutrality of Salts and Coloured Indicators. By HENRI LESCŒUR (*Compt. rend.*, 1896, **123**, 811—813).—The author discusses the precise significance of the colour changes of certain indicators. He points out that the formation of a blue colour with litmus indicates the presence of excess of alkali, and not neutrality. When an alkali is added to a solution of a salt of an insoluble oxide in presence of litmus, the change to blue takes place, not when all the free acid has been neutralised, but after all the oxide has been precipitated and the alkali is in excess. In many cases, the colour of the litmus changes continuously from red to blue. The behaviour of litmus with alum and other salts clearly shows that the red colour indicates neutrality as well as acidity.

In the case of phenolphthalein, the production of the red colour indicates, not the passage from acidity to alkalinity, but from neutrality to alkalinity.

Helianthin (Poirrier's orange No. 3) is colourless in neutral or alkaline solutions, and red in presence of acids. This indicator, therefore, shows the passage from neutrality to acidity.

The author considers that a really neutral substance is one with which phenolphthalein and helianthin both remain colourless, whilst litmus remains red. C. H. B.

Speed of Etherification, as compared with Theory. By ROBERT B. WARDER (*J. Physical Chem.*, 1896, 1, 149—156).—The theory of mass action is applied to Lichty's experiments (Abstr., 1896, ii, 557) on the speed of etherification, in which equivalent weights of ethylic alcohol and the several chloracetic acids were made to react for definite intervals at 80°. Numbers are given proportional to the coefficient of speed, as obtained by integration between the limits of successive determinations. They show the same general features for each acid; a steady decrease in the early stages is followed by a moderate increase, then by a rapid fall. Further experiments are needed to determine the cause of the secondary influences indicated before the actual constants can be determined and in order to trace the effect of successive atoms of chlorine in acetic acid. H. C.

Catalytic Hydrolysis by Metals. By BOHUSLAV RAYMAN and OTTOKAR ŠULC (*Zeit. physikal. Chem.*, 1896, **21**, 481—492).—The effect of temperature on the inversion of sugar by pure water was first studied, a platinum flask provided with a reflux platinum condenser being employed. At 60°, no change occurred in 50 hours; at 80°, the rotation fell from $+11{\cdot}56°$ to $+0{\cdot}31°$ in 58 hours, and at 100° reached $-3{\cdot}42°$ in 25 hours. Rotation/time curves are constructed in each case, from which it is seen that the velocity of inversion is at first

small, then increases, and again diminishes towards the close of the reaction. In glass vessels, the velocity is considerably less, and the effect of metals other than platinum was, therefore, investigated by the use of similar copper and silver flasks, when the rate of inversion was found to be slightly less than in the platinum vessel and less in the copper than in the silver flask. The solution in the copper flask became slightly acid and turbid owing to traces of finely-divided copper. The effect of finely-divided metals of the platinum group was investigated, hard glass flasks being used, and curves are given as before. An increase of velocity was obtained in each case, except that of iridium, the accelerative effect of palladium being extraordinarily great. The effect is probably due partly to a specific action of the metal and partly to acids formed by oxidation. The decomposition of glucose and fructose by water was therefore investigated, but found to be of a very complicated nature. L. M. J.

Absorption. Water in Colloids, especially in the Hydrogel of Silicic Acid. By JACOBUS M. VAN BEMMELEN (*Zeit. anorg. Chem.*, 1896, **13**, 233—356).—In continuation of his researches on the composition and properties of inorganic oxides in the colloidal state (Abstr., 1894, ii, 191), the author has examined the conditions under which the absorption and elimination of water by the hydrogel of silicic acid take place at constant temperature. The process is a gradual and a continuous one, the elimination of water taking place, however, with greater difficulty the more nearly the substance approaches the anhydrous condition. The hydrogel appears to form an intermediate stage in the passage from the liquid to the solid condition during the separation of a dissolved colloidal substance from a solvent. This separation commences with the formation of the hydrosol, the solution usually remaining clear, but the dissolved substance exercising little or no influence on the osmotic pressure, boiling point, freezing point, or electrical conductivity. Solutions of colloids in this condition contain molecular groups which do not follow the laws which hold for crystalloids in solution, and determinations of the molecular weights of colloids in solution by the customary methods are therefore valueless. The formation of the hydrogel is indicated by the coagulation that occurs. It may be assumed that the semiliquid particles of the colloid arrange themselves with the water molecules to form a cell-like structure of definite form, and that these cells hang together at certain points, so forming a network. The water is then retained, partly by the cells themselves, and partly in the interstices between the cells. The author shows that the general behaviour of the hydrogel of silicic acid is in keeping with these views. H. C.

Theory of Corresponding States. By G. BAKKER (*Zeit. physikal. Chem.*, 1896, **21**, 507—508).—The paper contains a more rigid proof of the conclusions obtained in the author's previous paper (this vol., ii, 17) which involved certain tacit assumptions. L. M. J.

Unit of Atomic Weights. By KARL SEUBERT (*Zeit. anorg. Chem.*, 1896, **13**, 229—232).—The author regards the result of Morley's

determination of the ratio O : H = 15·879 : 1 as probably correct to within 0·06 per cent. It may, therefore, now be regarded as proven that the atomic weight of oxygen (H = 1) is, for practical purposes, about 15·88. The use of this number, and the retention of the atomic weight of hydrogen as the unit, is advocated in place of the practice of fixing the atomic weight of oxygen as 16. H. C.

The Discovery of New Elements during the last Quarter of a Century, and Questions relating thereto. By CLEMENS WINKLER (*Ber.*, 1897, **30**, 6—21).—This paper is the report of a lecture delivered before the German Chemical Society, and traces the history of those elements which have been discovered during the last quarter of a century. M. O. F.

A New Stirrer. By HERMANN SCHULTZE (*Ber.*, 1896, **29**, 2883).—This consists of a glass rod, to one end of which two glass balls are hung by pieces of platinum-iridium wire. When the rod is rotated by a turbine, the balls fly asunder, stirring the liquid in which they are immersed. C. F. B.

Inorganic Chemistry.

Nascent Hydrogen. By R. Franchot (*J. Physical Chem.*, 1896, 1, 75—80).—Ferric sulphate was reduced in an electrolytic cell, using platinum as the cathode, and pure zinc, cadmium, or copper as the anode. As, on analysis, it was found that the reduction at the anode was equal to or even greater than that at the cathode, it became evident that zinc, cadmium, and copper reduce ferric sulphate directly. This was further confirmed by adding zinc, cadmium, and copper, to different portions of a carefully neutralised solution of ferric sulphate, when in all three cases considerable quantities of ferrous iron were formed. It appears, therefore, that, in the reduction of ferric salts in acid solutions by metals, there is a direct reduction by the metal and an indirect reduction due to the action of the acid on the metal. H. C.

Action of Sulphuric Acid on Iodine and Iodic Acid. By Paul Chrétien (*Compt. rend.*, 1896, **123**, 814—816).—When iodic acid is dissolved in sulphuric acid at 200°, there is slight decomposition, and the crystals that separate on cooling are yellowish, but if some fuming nitric acid is added to the hot liquid, the crystals are white. They retain small quantities of sulphuric acid when dried on porcelain, but, if powdered and again dried, they contain 99·6 per cent. of iodic anhydride; this has not previously been obtained in a crystalline form.

When the solution of iodic acid in sulphuric acid is heated at 250—260°, oxygen and iodine are liberated, and a yellow, amorphous precipitate is formed which is instantly decomposed by water into iodine, iodic acid, and sulphuric acid. With prolonged heating, the liquid becomes black, and then, with extreme slowness, it deposits yellow crystals, which can also be obtained by dissolving iodine in a

hot solution of iodic acid in sulphuric acid. These crystals are decomposed by water in the same way as the amorphous products. The ratio of iodine to oxygen is 5·291, and of free iodine to iodine present as iodic acid 1·506. The crystals seem to have the composition

$$2SO_3,H_2O,2I_2O_3;$$

they are decomposed by water in accordance with the equations

$$3I_2O_3 + H_2O = 2I_2O_5 + 2HI \text{ and } I_2O_5 + 10HI = 6I_2 + 5H_2O,$$

the final result being $5I_2O_3 = 3I_2O_5 + 2I_2$.

Ogier found that the action of ozone on iodine converts it into a yellow powder, which is decomposed by water in the same way as the compounds described by the author. C. H. B.

Ozone and Phosphorescence. By Marius Otto (*Compt. rend.*, 1896, **123**, 1005—1007).—Whilst ozonised air was being aspirated with a water pump, it was observed that the water became luminous, and retained its luminosity for five or six seconds. Flasks filled with the issuing water were, in fact, distinctly luminous.

It was found that, when water is shaken with ozonised oxygen, the phenomenon of luminescence can be reproduced five or six times and then ceases, but is observed again with the same quantity of gas if a fresh quantity of water is introduced. Increase or reduction of pressure has no appreciable effect on the luminosity. With alcohol of 90°, the luminescence is feebler but more persistent; with benzene, it is very feeble, and the ozone is completely absorbed or decomposed.

Thiophen yields abundant luminous vapours, and is the only compound that showed this peculiar phenomenon. With milk, the phosphorescence is much more intense than with ordinary water, and with urine, it was more intense than with any other compound examined. On the other hand, water carefully freed from organic matter showed no phosphorescence, even with highly concentrated ozone, and it follows that the phosphorescence observed with ordinary water is due to the action of the ozone on the vegetable or animal matter present in it. C. H. B.

Action of some Hydrogen Compounds on Thionyl Chloride. By J. Adolphe Besson (*Compt. rend.*, 1896, **123**, 884—886).—Aluminium bromide reacts vigorously with thionyl chloride, the solution, when cooled, depositing crystalline double compounds of aluminium chloride and bromide with thionyl chloride; on distilling this under reduced pressure, thionyl bromide, solidifying at −52°, is obtained, but the yield is much smaller than is obtained by the method previously described by the author (Abstr., 1896, ii, 358). Hydrogen iodide reacts vigorously with thionyl chloride, according to the equation $2SOCl_2 + 4HI = 4HCl + 2I_2 + SO_2 + S$, even when cooled by a freezing mixture.

Hydrogen sulphide reacts slowly with thionyl chloride, according to the equation $2SOCl_2 + 2H_2S = 4HCl + SO_2 + 3S$, when cooled in a mixture of ice and salt, whilst at higher temperatures the main action is represented by the equation $2SOCl_2 + H_2S = S_2Cl_2 + SO_2 + 2HCl$. Gaseous hydrogen phosphide at ordinary temperatures causes an evolution of hydrogen chloride, the liquid, after some time, forming two

layers, the upper of which, on distillation under reduced pressure, yields, first, thionyl chloride, then phosphoryl chloride, and, finally, thiophosphoryl chloride, $PSCl_3$; a syrupy liquid from which no definite compound can be obtained remains in the retort. The lower layer is viscous, and contains chlorine, sulphur, phosphorus, oxygen, and hydrogen. It yielded no definite results on analysis.

A. C. C.

Densities of Nitrogen, Oxygen, and Argon, and the Composition of Atmospheric Air. By ANATOLE LEDUC (*Compt. rend.*, 1896, **123**, 805—807).—The author's determination of the density of nitrogen prepared by chemical methods gives 0·9671 as compared with air. Oxygen obtained by electrolysis of a solution of potassium hydroxide gives the number 1·10523, which is slightly lower than that previously given. The density of argon calculated from the density of air, and the constant proportion (0·0119) of argon in it, is 1·376, or 19·8 with reference to hydrogen.

The weight of a litre of oxygen at 0° and normal atmospheric pressure is 1·4293 grams; of nitrogen, 1·2507 grams; and of argon, 1·780 grams.

The composition of air by weight is, nitrogen, 75·5; oxygen, 23·2; argon, 1·3; and, by volume, nitrogen, 78·06; oxygen, 21·0; and argon, 0·94.

C. H. B.

Presence of Nitrites in the Air. By GEORGE DEFREN (*Chem. News*, 1896, **74**, 240—241).—Continuing these investigations (compare this vol., ii, 94), air tightly corked up for 12 to 24 hours in large bottles of over 8 litres capacity along with 100 c.c. of water, and occasionally shaken, yielded up all its nitrites to the water. Determinations made in this way showed that the presence of human beings in a room increases the proportion of nitrites in the air, and confirmed the similar effect of burning gas already noticed. Air from the lungs blown through water gave no evidence of nitrites; this, however, is not considered conclusive evidence of the absence of nitrites in expired air, inasmuch as air that yields nitrites when exposed over water, does not yield them when bubbled through water, this being attributed to the oxidation of the nitrites to nitrates by the large preponderance of oxygen in the gaseous mixture. Like previous investigators, the author finds the proportion of nitrites and nitrates in the air increased by thunderstorms, and reduced, by washing out, by rainstorms.

D. A. L.

Transformations of Pyrophosphoric Acid. By MARCELLIN BERTHELOT and GUSTAVE ANDRÉ (*Compt. rend.*, 1896, **123**, 776—782).—A solution of pyrophosphoric acid containing 15·6 grams of phosphoric anhydride per litre was prepared by the action of hydrogen sulphide on lead pyrophosphate, and was allowed to remain at the ordinary temperature, the proportion of pyrophosphoric acid being determined from time to time (this vol., ii, 158). Titrations with tropeolin and phenolphthalein showed that the solution contained no metaphosphoric acid, and that none of the latter was formed during the course of the experiments. One series of the experiments gave the following results.

Days	2	5	10	19	52	89	110	121
Percentage of pyrophosphoric acid remaining	91	87	83	76·5	69·5	58	49·5	43·1.

The conversion of pyrophosphoric into orthophosphoric acid proceeds continuously, but is very much slower than the hydration of metaphosphoric acid. Experiments with a solution of half the concentration gave similar results, and showed that the rate of change increases with the concentration. Similar results were obtained with pyrophosphoric acid prepared by the action of hydrochloric acid on silver pyrophosphate.

In order to ascertain whether pyrophosphoric acid can be obtained by the direct dehydration of the ortho-acid, some of the latter was heated and weighed from time to time, and when the ratio of phosphoric anhydride to water was 1 : 1·55, the product contained 56·4 per cent. of the phosphorus as pyrophosphoric acid, 29·8 per cent. as the ortho-acid, and 13·8 as the meta-acid. It follows that some metaphosphoric acid is formed even before all the ortho-acid has been converted into the pyro-acid, and, during the heating, a condition of equilibrium is established between the three acids. When the heating is carried further, the phenomena become very complex, owing to the polymerisation of the meta-acid. During the heating, there is a notable volatilisation of the solid matter, which, however, only becomes distinct when the meta-acid begins to form. C. H. B.

Effect of the Presence of Boric Acid in Glass and Enamels. By L. GRENET (*Compt. rend.*, 1896, **123**, 891—893).—When boric acid is added to glass and enamels, it increases their toughness and fusibility, and modifies their coefficient of expansion, sometimes increasing and at other times diminishing it. When increasing quantities of boric acid are added to glass, the coefficient of expansion at first diminishes and then increases, finally approaching that of boric acid itself.

Tables are given showing the coefficients of expansion of mixtures of the oxides of sodium, lithium, zinc, and lead, as also of white glass and bottle glass, with increasing quantities of boric acid. The amount of boric acid that can be added to glass without causing devitrification, on the one hand, or the separation of the added boric acid, on the other, depends on the nature of the metallic oxides and the proportion of silica contained in the glass, as well as on the rapidity with which the latter is cooled. A. C. C.

Combustion of Illuminating Gas on Cooled Surfaces. By FRITZ HABER and A. WEBER (*Ber.*, 1896, **29**, 3000—3006).—According to Lewes (Abstr., 1892, 407), appreciable quantities of unburnt gas arise from the combustion of illuminating gas on cooled surfaces; the authors, however, consider that this result is due to an insufficiency of oxygen, and have, therefore, repeated the investigation. They state the results of numerous experiments carried out with a Teclu gas-burner and with various forms of gas-stove, and appear to arrive at the same conclusion as Lewes. An explanation of the presence of unburnt gas is put forward in the paper. M. O. F.

The Development of the Soda Manufacture and Allied Industries in the last 25 Years. By ROBERT W. HASENCLEVER (*Ber.*, 1896, **29**, 2861—2877).—This period stretches roughly from the development of the ammonia-soda process to the realisation of an electrolytical method for the preparation of soda. The paper under review contains very brief notices of the more important innovations during this period, and gives references to sources where details of the methods introduced may be found.

Sulphuric Acid manufacture.—Pyrites is still the chief source of the sulphur. The German ore, the consumption of which has remained fairly constant, contains zinc, and this is recovered from the roasted ore by an electrolytical method. Spanish ore is more and more imported into Germany; 1 ton of it yields 610 kilos. of iron oxides, 34 kilos. of copper, $29\frac{1}{2}$ grams of silver, and $\frac{1}{10}$ gram of gold. Some works are erecting blast-furnaces for smelting the iron oxides, which they find a difficulty in selling. A successful method of utilising zinc blende for the manufacture of sulphuric acid has also been worked out. In the construction of the leaden chambers, of the acid pumps, and of other apparatus, great advances have been made, the chemist having called in the engineer to his aid. Lunge, guided by some of his researches, has even proposed to substitute earthenware towers with perforated plates for the leaden chambers. The chamber acid is still concentrated at first in leaden pans, the final concentration being carried out, as a rule, in platinum vessels on the Continent, whilst in England glass vessels are still largely used. Lunge has patented a method by means of which a concentrated acid is made, by cooling it to about $-20°$, to yield crystals of H_2SO_4, a weaker acid beng left behind. Sulphuric anhydride is now made on the large scale, and cheaply; the best way is to obtain a solution of sulphurous anhydride by passing through water the gases given off from the furnaces in which pyrites is roasted, to heat this solution, and pass a mixture of the evolved gas with air under increased pressure over platinised asbestos.

Hydrochloric Acid and Chlorine.—On the Continent, where the ammonia-soda process has almost entirely replaced the old Leblanc process, the price of hydrochloric acid has risen greatly, and certain branches of industry that depended on it have had to be given up. In England, however, no great rise in price has taken place, so that, in this country, chlorine is still largely made by the Weldon process, although the Deacon process has of late begun to find a wider development; the latter process is now the one chiefly used on the Continent. One of its defects is, that the conversion of the hydrogen chloride is not complete, and a weak solution of this gas is obtained as a bye-product; the use of sulphuric acid has been introduced to regenerate the gas from this solution.

The ammonia-soda manufacturers have made many attempts to obtain chlorine from the bye-products formed in that process. The only method which has been attended with any measure of success is that of Mond, who freezes out the ammonium chloride from the solution of it obtained in working the ammonia-soda process, volatilises it in vertical cast-iron retorts lined with thin tiles, passes the vapour into vertical wrought-iron cylinders packed with balls of magnesia (containing a little kaolin and calcium chloride) heated to a temperature of 300°, and drives out the

ammonia by means of the gases resulting from the calcination of sodium hydrogen carbonate; these gases contain no oxygen, and being heated by passing first through a regenerator, they raise the temperature of the magnesia decomposer to 600°. Air is then passed into the decomposers at this temperature, and a gas containing 18—20 per cent. by volume of chlorine is obtained; finally, the decomposers are cooled to 350° by a current of cold air, and ammonium chloride vapour is then again introduced. As regards the chemical reactions involved, the ammonium chloride vapour reacts with the magnesia, yielding magnesium chloride, together with ammonia and water, which pass on. The magnesium chloride is then decomposed by the oxygen of the air, chlorine being formed and magnesia regenerated. Mond is, however, not extending this process as rapidly as he would otherwise have done, on account of the introduction of electrolytical methods for the preparation of chlorine. In the manufacture of bleaching powder, mechanical methods have been largely introduced; lime, fed in at one end of a system of pipes, is made to travel through these by an endless screw, meeting a current of chlorine as it does so, and is delivered as bleaching powder at the other end of the system.

Soda.—In Germany, France, Austria, and England, 13, 16, 36, and 50 per cent. respectively of the total output is still manufactured by the old Leblanc method; in this method, the chief advance consists in the introduction of mechanical furnaces, in place of working the charges by hand. Hargreaves has developed a method by which sodium sulphate is made directly, without the intervention of sulphuric acid, by the action of sulphurous anhydride, steam, and air on salt in iron cylinders; the products are sodium sulphate and hydrochloric acid. This process is worked to some extent in England, and also at one or two works in France and Germany. The recovery of the sulphur from the waste of the Leblanc process was at one time effected by letting the waste stand with water in tanks through which air was blown, and then decomposing the resulting extract with hydrochloric acid, when sulphur was precipitated. This process, due to Schaffner and Mond, is now less used, on account of the rise in price of hydrochloric acid. Chance has worked out a process in which the soda waste is treated in cylinders with the gases obtained by burning limestone; hydrogen sulphide is formed, and this is burned to sulphur and water in a Claus furnace, whilst the calcium carbonate remaining in the cylinders is used for making cement. This method is worked in England, but not very widely. In the ammonia-soda process, the chief advances have been in the increase of the output of an installation, and in diminishing the loss of ammonia.

C. F. B.

Lithium Nitride. By ANTOINE GUNTZ (*Compt. rend.*, 1896, **123**, 995—997).—Lithium combines with nitrogen with incandescence when heated in a stream of the gas, but the product is impure, because the dish holding the lithium is attacked. Iron, nickel, silver, platinum, rock crystal, and graphite are all acted on somewhat readily. A much purer product is obtained by heating the lithium very gently in an iron dish in a very slow current of nitrogen, but in this case some of the lithium may remain uncombined. It is very important to take account of impurities in calculating the results of the thermochemical

measurements. When this allowance is made, the product has the composition Li_3N, and the reaction $Li_3N + nH_2O$ liq. = 3LiOH diss. + NH_3 diss. develops +131·1 Cal., and hence 3Li sol. + N gas = Li_3N sol. develops +49·5 Cal. This value is lower than the heat of combination of lithium with hydrogen (+21·6 Cal. for Li), and, as a matter of fact, the nitride is decomposed somewhat easily when heated in hydrogen.

On the other hand, the hydride seems to be decomposed when heated in nitrogen, but what really happens is that the hydride dissociates and the nitrogen then combines with the liberated lithium.

C. H. B.

Beryllium Oxide. By PAUL LEBEAU (*Compt. rend.*, 1896, **123**, 818—821).—Pure beryllium oxide, prepared by the method previously described (Abstr., 1896, ii, 168), fuses in the electric arc, and, on cooling, forms a white, crystalline mass, slightly harder than rubies. On the surface, there are often small, detached hexagons, resulting from condensation of vapour of the oxide, which, therefore, is somewhat volatile in the arc. The sp. gr. of the oxide dried at 440° is 3·012 at 0°, and that of the fused oxide 3·025 at 0°; it follows, therefore, that no appreciable polymerisation takes place at a high temperature. The fused oxide is not attacked by gaseous hydracids at a red heat, but concentrated acids dissolve it slowly, and in this respect it differs from alumina. In sulphuric acid, it swells up and yields a dense crystalline powder of anhydrous beryllium sulphate, which dissolves very slowly in boiling water.

The oxide dried at 440° is attacked by fluorine when heated, but not by other halogens or by members of the sulphur and nitrogen groups. In the electric furnace, it is reduced by carbon, silicon, or boron and with the latter yields a crystallised boride mixed with carbon boride and a beryllium borocarbide. Potassium, sodium, and aluminium have no action on the oxide at high temperatures, and it is not reduced by magnesium, even at the boiling point of this metal.

C. H. B.

Earths of the Yttria Group in Monazite Sands. By PAUL SCHÜTZENBERGER and O. BOUDOUARD (*Compt. rend.*, 1896, **123**, 782—788. Compare Abstr., 1896, ii, 475).—The authors have fractionated the earths of the yttria group obtained from monazite sands, by means of fractional crystallisations of the sulphates and fractional decomposition of the nitrates. They find that after the former method has yielded an oxide of constant molecular weight, the latter allows it to be still further fractionated. Details of the fractionations are given; the extremes of the molecular weights of the oxides are 91·25 and 148, but both the extremes and all the intermediate fractions give the same spark spectrum, consisting chiefly of two bands at λ618—614, and λ602—595·5, with further bands at λ499—497·5 and λ481·5—480. These spectra seem to be identical with that of yttria, but the high equivalent of some of the fractions of oxides show that they are not identical with yttria. C. H. B.

The Alleged New Element, Lucium. By WILLIAM CROOKES; (*Chem. News*, 1896, **74**, 259).—Careful physical and chemical examina-

tions, revealed the fact that P. Barriere's lucium was nothing but impure yttrium. D. A L.

Reduction of Permanganic Acid by Manganese Dioxide. By HARMON N. MORSE (*Ber.*, 1897, **30**, 48—50. Compare Abstr., 1896, ii, 475).—The results already described (*loc. cit.*) are again enumerated (compare Hirtz and Meyer, this vol., ii, 93). In the spontaneous liberation of oxygen due to precipitated manganese dioxide, the author recognises a tendency to the production of substances forming a homologous series $MnO,5MnO_2$, $MnO,10MnO_2$, $MnO,15MnO_2$, differing by $5MnO_2$.

In presence of nitric acid, lead peroxide and permanganic acid both lose oxygen in accordance with the equation $2HMnO_4 + 3PbO_2 = H_2O + 2MnO_2 + 3PbO + 3O_2$. M. O. F.

The Tempering of Steel in a Solution of Phenol. By LEVAT (*Compt. rend.*, 1896, **123**, 945).—Steel tempered in a solution of phenol possesses greater hardness, elasticity, and flexibility than when tempered in water. A. C. C.

Absorption of Nitric Oxide by Ferrous Bromide. By VICTOR THOMAS (*Compt. rend.*, 1896, **123**, 943—945).—The author has determined the amount of nitric oxide absorbed by known weights of ferrous bromide dissolved in known volumes of water at 10°, and at 15—16°. At the lower temperature, two experiments gave results agreeing with the formation of a compound of the formula $3Fe_2Br_4,4NO$. At the higher temperature, the absorption corresponded with the formation of a compound of the formula Fe_2Br_4,NO. These results are confirmatory of those obtained by Gay with ferrous sulphate and chloride, who found that, below 12·5°, 3 atoms of iron united with 2 molecules of nitric oxide, whilst above that temperature 2 atoms of the metal united with 1 molecule of the gas. In a future communication, the author will describe a crystalline compound obtained by the union of nitric oxide with ferrous bromide in ethereal solution.
A. C. C.

Crystallised Magnesium Chromite. By EM. DUFAU (*Compt. rend.*, 1896, **123**, 886—888).—When a mixture of chromium sesquioxide (150 grams) and magnesium oxide (40 grams) is heated in the electric furnace with an arc of 50 volts and 300 ampères, normal magnesium chromite, $MgCr_2O_4$ is formed which can easily be obtained as a dark green, crystalline powder. The crystals, which are octahedral, have a sp. gr. = 4·6 at 20°, are harder than quartz, and have no action on polarised light. They are readily attacked by sulphuric acid, slowly by hydrochloric and hydrofluoric acids, and are not acted on by boiling nitric acid. Chlorine, bromine, iodine, and sulphur have no marked action on the compound, and it is oxidised only with great difficulty, even when heated to redness in oxygen or when fused with potassium chlorate or nitrate. Under the conditions of the experiment, no basic chromites were formed. A. C. C.

Molybdenum Iodide. By M. GUICHARD (*Compt. rend.*, 1896, **123**, 821—823).—When molybdenum chloride, obtained by the direct

action of chlorine on the metal, is heated in a current of hydrogen iodide, a considerable quantity of iodine is liberated and a brown, amorphous di-iodide, MoI_2, is formed, of sp. gr. 4·3 ; it is insoluble in water and alcohol. When heated in a vacuum up to the melting point of glass, it is not decomposed, but when heated in air, iodine is liberated and an oxide is formed which, at a higher temperature, is converted into molybdic anhydride. Hydrogen reduces the iodide at 500°, and the change is very rapid at an incipient red heat. Chlorine decomposes it below 240°, and bromine behaves similarly. In oxygen at 350°, there is vigorous incandescence, with liberation of iodine and formation of molybdic anhydride. Sulphur readily converts the iodide into a black sulphide, but nitrogen is without action at the softening point of glass. Water decomposes it very slightly at the ordinary temperature, and a little more rapidly at 700°, whilst in superheated steam, hydrogen is liberated as well as hydrogen iodide, probably as a result of the decomposition of the steam by an oxide, MoO, formed as the first product of the action of the steam on the iodide. Hydrogen sulphide converts the iodide into sulphide, and sulphuric and nitric acids oxidise it slowly in the cold and more rapidly on heating. Aqueous potash acts on it slowly at the ordinary temperature.

C. H. B.

Mineralogical Chemistry.

Artificial Pirssonite: Simultaneous Production of Northupite, Gaylussite, and Pirssonite. By AUGUST B. DE SCHULTEN (*Compt. rend.*, 1896, **123**, 1023—1025).—Bright, limpid crystals of the new mineral, pirssonite (this vol., ii, 48), have been artificially produced by adding excess of calcium chloride to a solution of sodium carbonate and heating the mixture on the water bath for 12 hours. The minute crystals are orthorhombic, and are tabular parallel to *b* (010), but do not show the hemimorphism which is so characteristic of the natural mineral; they have the optical characters of pirssonite. The composition is $CaCO_3,Na_2CO_3,2H_2O$; sp. gr. 2·349. At 100°, there is no change, but at 130°, most of the water is lost. When placed in water, the crystals soon become dull, and after a time are decomposed into calcium and sodium carbonates.

The new mineral, northupite, has already been artificially prepared by the author (Abstr., 1896, ii, 610). Northupite, pirssonite, and gaylussite all occur together at Borax Lake, California, and they have been prepared simultaneously by heating for some hours on the water bath a mixture of 150 grams of sodium chloride, 50 grams of sodium carbonate, 6 grams of calcium chloride, and 10 grams of magnesium chloride in 550 c.c. of water. By this method, octahedra of northupite and delicate needles of gaylussite are obtained, and, as the solution is concentrated, pirssonite is formed at the expense of the gaylussite. Rhombohedral crystals of the double salt $MgCO_3,Na_2CO_3$ (Abstr., 1896, ii, 610) are also formed at the same time, and it is predicted that this will be found as a natural mineral at Borax Lake.

L. J. S.

Anhydrite in Ontario. By W. NICOL (*Canadian Record Sci.*, 1896, 7, 61).—Anhydrite occurs in considerable quantity at the Foxton phosphate mine, township of Loughborough, Co. Frontenac. It is associated with gypsum, calcite, and pyroxene, and resembles pink fluorite in appearance. Analysis gave

CaO.	SO_3.	CO_2.	SiO_2.	Fe_2O_3.	Loss on ignition.	Total.
41·71	57·47	0·286	0·151	0·065	0·26	99·942

L. J. S.

Valleite, a new Orthorhombic Amphibole. By GIUSEPPE CESÀRO (*Bull. Acad. Sci. Belg.*, 1896, [3], 32, 536—545. Compare Abstr., 1896, ii, 481).—This mineral occurs with the violet tremolite (hexagonite) of Edwards, St. Lawrence Co., N.Y.; it closely resembles anthophyllite in appearance, but differs from it in its optical characters and in containing only a small amount of iron. The indistinct crystals are flattened parallel to (100) and have a perfect lamellar cleavage in this direction; other cleavages are (010), (021), and, less distinct, (110), (011), (031), and (001). The prism angle is 54° 30′; $a:b:c = 0·515:1:0·255$. The plane of the optic axes is (010), and the acute negative bisectrix is perpendicular to (100); 2E = 90° 28′. H = 4·5; sp. gr. 2·88. It is easily fusible to a white, nearly opaque, bead. Analysis by Renard gave

SiO_2.	MgO.	CaO.	Fe_2O_3.	MnO.	K_2O.	H_2O.	Total.
58·02	27·99	5·04	1·28	2·88	0·89	3·13	99·23

This agrees with the metasilicate formula, RO,SiO_2. L. J. S.

The Garnet Group. By H. SCHNERR (*Zeit. Kryst. Min.*, 1896, 27, 431—432; from *Inaug.-Diss.*, *München*, 1894).—Several analyses are given of the lime-garnets associated with the serpentine masses of the Eastern Alps; some of these have been quoted by Weinschenk (this vol., ii, 106). The following are of garnets from the Rothenkopf, Zillerthal, Tyrol: I, light red; II, cherry-red; III, dark brown.

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	Total.
I.	37·18	14·03	13·73	2.54	trace	32·73	100·21
II.	36·75	6·90	21·38	2·17	trace	32·55	99·75
III.	37·52	13·29	13·01	1·71	0·54	34·01	100·08

As in the garnets of the Gross-Venediger, the dark brown shows the more marked optical anomalies, whilst the cherry-red is almost isotropic. From the analyses, it is seen that there is no connection between colour and chemical composition, and that the darker garnets (aplome) are not richer in ferric oxide than the lighter (essonite), as is sometimes supposed. L. J. S.

[Action of Hydrochloric Acid on Titaniferous Augite.] By E. LORD (*Zeits. Kryst. Min.*, 1896, 27, 431; from *Inaug.-Diss.*, *Heidelberg*, 1894).—In a dissertation on the basalts of the Fichtelgebirge the following analyses of the zoned titaniferous augite from the limburgite of the Kaiserstuhl, Baden, are given; these were made with the object of seeing whether, by the action of hydrochloric acid, a separation into parts containing titanium and free from titanium could be effected. The bulk analysis of the augite is given under I; II gives the com-

position of the portion (57 per cent. of the whole) which went into solution when the powdered mineral was digested for 12 hours with hot, concentrated hydrochloric acid; and III gives the composition of the insoluble portion.

	SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MgO.	CaO.	Na_2O.	K_2O.	Total.
I.	43·85	3·14	6·19	6·99	3·70	11·89	22·44	1.50	0·50	100·20
II.	43·41	3·19	6·92	7·04	3·38	11·64	22·54	1·50	0·50	100·12
III.	44·30	3·09	5·46	6·85	4·04	12·75	22·34	[1·17]		100·00

After digesting for 4 days, 82·44 per cent. was dissolved; and with dilute acid (1 : 1), 43·77 was dissolved after 12 hours. In both these cases, the composition of the soluble and insoluble portions is, as before, much the same as that of the original augite, so that no separation can be effected by these means. L. J. S.

Endomorphic Alterations of Granitic Magma in Contact with Limestone. By ALFRED LACROIX (*Compt. rend.*, 1896, **123**, 1021—1023).—At the peak of Braceil, in Orlu, Ariège, the granite of Quérigut is in contact with a thick, sedimentary series consisting of schists with thick bands of limestone. Fragments of the schist and limestone are enclosed in the granite, and these rocks have been largely absorbed by the granitic magma. The granite in contact with the extensively corroded limestone has undergone considerable alterations; it becomes progressively more basic, by loss of quartz and felspar, and development of hornblende and mica, and lastly olivine, and passes to hornblende granite, quartz-diorite, mica-diorite, hornblendite, and, finally, to hornblende-peridotite, this being an almost complete series of granular eruptive rocks. Sometimes enstatite is developed, and norites, with or without olivine, result. The plagioclases, oligoclase to anorthite, are zoned and much corroded, indicating great variations in the composition of the magma. L. J. S.

Gas from the Mineral Waters of Bagnoles de l'Orne. By CH. BOUCHARD and ALEXANDRE DESGREZ (*Compt. rend.*, 1896, **123**, 969—970).—The gas from the mineral waters of Bagnoles de l'Orne contains carbonic anhydride, 5·0; nitrogen, 90·5; argon, 4·5; helium, traces = 100·00. No carbonic anhydride is found in the mineral waters of Cauterets. C. H. B.

Mineral Water of Kralitz. By FR. FAKTOR (*Verh. naturf. Ver., Brünn*, 1896 (1895), **34**, 366—368).—The baths of Kralitz, near Prossnitz, in Moravia, have been known since 1825. The water has a temperature of 9°; sp. gr. = 1·00544 at 16·5°; on standing, it becomes turbid, and deposits ferric oxide, silica, and organic matter. Analysis gave, in 1,000,000 parts :—FeO, 18·526; CaO, 158·400; MgO, 41·656; K_2O, 32·118; Na_2O, 44·961; SiO_2, 15·600; SO_3, 36·382; P_2O_5, 0·260; Cl, 50·763; CO_2, in bicarbonates, 330·110; CO_2, free, 9·073; total solids (dried at 180°), 562·029. L. J. S.

Physiological Chemistry.

Mercury Air Pump for the Estimation of Blood-Gases. By FRIEDRICH NEESEN (*Zeit. physiol. Chem.*, 1896, **22**, 478—482).—This is a modification of the mercurial air pump, the details of which are fully explained, and illustrated by a diagram. The special advantage claimed for it is rapidity of action. W. D. H.

Gastric Digestion. By FERDINAND KLUG (*Pflüger's Archiv.*, 1896, **65**, 330—342).—A large number of albuminous substances were subjected to the action of gastric juice prepared from the dog, pig, and ox, and the results compared. Differences between the three juices occur; but the main result is that alkali-albumin and casein are best digested, after these follow serum-albumin, syntonin, serum-globulin, fibrin and legumin; whilst boiled egg-albumin and dry meat powder are the least easily digestible. The yield of anti-albumose is greatest with alkali-albumin and plant-casein; then follow serum-globulin, syntonin, serum-albumin, and casein. The yield of hemi-albumose is greatest with casein, both animal and vegetable; serum-albumin, syntonin, gluten, and gluten-fibrin also yield a relatively large amount of hemi-albumose; serum-globulin, fibrin, boiled egg-white, legumin, and raw flesh yield relatively little. On the other hand, serum-globulin and syntonin yield the most peptone; egg-albumin, casein, serum-albumin, and fibrin follow in the order named.

Another series of tables gives the effects of different acids. The absolutely greatest quantity of proteid is dissolved by pepsin in the presence of hydrochloric and lactic acids; phosphoric, nitric, acetic acids follow, and then, at a distance, sulphuric and citric acids. The optimum concentration differs with the different acids; thus it is 0·6 for hydrochloric, 8·0 for lactic, 6·0 for phosphoric and acetic, 0·8 for nitric, 0·6 for sulphuric, and 8·0 for citric acid. The relative proportion of hemi- and anti-products differs considerably with the various acids, a fact which is against the supposition that the hemi- and anti-group exist preformed in the albuminous molecule. W. D. H.

The Blood of New-born Animals. By HUGO WINTERNITZ (*Zeit. pysiol. Chem.*, 1896, **22**, 449—477).—The blood of the fœtus, and of the new-born animal, is much richer in hæmoglobin and total solids than that of the adult animal, but shortly after birth this large proportion begins to diminish. The experiments recorded were made on dogs, cats, and rabbits, the hæmoglobin being estimated by the Hoppe-Seyler double pipette. W. D. H.

A New Enzyme in the Blood. By MAURICE HANRIOT (*Compt. rend.*, 1896, **123**, 753—755. Compare Abstr., 1892, 742).—The object of this investigation was to determine the manner in which reserve fat passes into the circulation and is utilised by the organism. In his experiments, the author, instead of employing the natural fats, makes use of an aqueous emulsion of monobutyrin as a test for the presence of a hydrolysing enzyme, on account of the greater ease with which

it is capable of undergoing saponification. Monobutyrin is readily saponified by blood serum in neutral or slightly alkaline solutions, but the action is considerably retarded by the presence of the liberated acid if this be left unneutralised. Using equal quantities of butyrin, the acidity in a given time is directly proportional to the amount of serum employed; moreover, the activity of the latter is destroyed when it is heated to 90°, it being then unable to produce butyric acid in the test solution. The amount of saponification taking place with various proportions of butyrin and serum in different times was determined by observing the quantity of a standard solution of sodium carbonate necessary to neutralise the liberated butyric acid; and the results are given in a table. The active enzyme, for which the name *lipase* is suggested, is also capable of acting, though much more slowly, on the natural oils and fats. *Lipase* is very stable, and appears to be as active in the serum at the end of eight days as at the beginning. In a future communication, the author proposes to show the invariable presence of lipase, both in plants and animals, whenever there is a reserve of fat to be utilised. A. C. C.

Fat in the Blood during Hunger. By Fr. N. Schulz (*Pflüger's Archiv.*, 1896, **65**, 299—307).—The experiments were made on rabbits, pigeons, and dogs. The fat was estimated by extraction with ether after preliminary artificial gastric digestion. Inanition was found to cause a rise of from 30 to 100 per cent. in the amount of fat in the blood, as compared with that in normal animals. W. D. H.

Absorption of Fats. By B. Moore and D. P. Rockwood (*J. Physiol.*, 1897, **21**, 58—84).—The emulsibility of free fatty acids, and their solubility in bile, have been known for many years, but the extent of such solubility has not been ascertained, and the bearing of these facts on fat absorption has not attracted much attention. The present research attacks both these points. In connection with the first, the solubility determinations show: (1) that palmitic and stearic acids are practically insoluble in ox bile at 38—40°, whilst 4 per cent. of oleic acid is easily soluble at that temperature. Hence the solubility of mixed fatty acids is probably due to an action of oleic acid in aiding the solution of the others. (2) Of the mixed fatty acids of lard, beef suet, and mutton suet, lard acids are most, and mutton suet acids least, soluble, the solubilities for the three sets being 3·5, 2·5, and 2 per cent. respectively in ox bile, 5, 5, and 1 in pig's bile; and 6, 5·5, and 2 in dog's bile. (3) The solubility of the fatty acids in bile is only in part due to bile-salts. Strong solutions of the bile-salts dissolve fatty acids much more feebly than the bile itself. Mere removal of the pseudomucin from bile diminishes its solvent action. A solution of pseudomucin alone, however, does not dissolve fatty acids. (4) On cooling the solution of fatty acids in bile below 40°, much of the dissolved acids separates out. The power of the bile to dissolve fatty acids is not impaired by repeating the process; the formation of a true emulsion was never observed.

The intestinal contents of the dog dissolve fatty acids in a way very similar to bile. Pancreatic juice and bile together decompose and dissolve fat; pancreatic juice alone decomposes, but does not

dissolve it, whilst bile alone has no action. A large number of experiments were made on the reaction of the intestinal contents in different animals, and the results and conclusions drawn therefrom may be summarised as follows.

The way in which fat is absorbed varies in different species of animals, and certainly it is not always absorbed as dissolved fatty acids. Most, however, if not all, of the fat is absorbed in soluble form by the epithelial cells, either as fatty acid or soap. When fatty acids are dissolved in bile or the mixed intestinal juices, the reaction of the solution is acid. Intestinal contents, therefore, which are alkaline to litmus cannot contain free fatty acids in solution. In white rats, the reaction is alkaline to litmus along nearly the whole small intestine, and usually the whole way, and, in the dog, the same is usually the case for the lower part of the ileum. Yet lacteals filled with white emulsion are seen proceeding from these parts. Here, probably, the fat is absorbed as soap.

In the greater part of the dog's small intestine, the reaction is acid to litmus, but alkaline to methyl-orange. The acidity to litmus is due to organic, probably dissolved fatty, acids, but the alkalinity to methyl-orange indicates that there is an excess of alkali above that required to combine with inorganic acids, and that this excess is combined with weak acids, probably with fatty acids in the form of soaps.

Munk objected to the view that any considerable amount of fat is absorbed as soap, on two grounds: (1) the acid reaction of the intestinal contents; (2) the enormous quantity of alkali which would be necessary to saponify all the fat in even an ordinary meal. The first objection falls to the ground when one considers that the acidity is due to organic acids; and the second may be met by the suggestion that a small amount of alkali could act as the mere carrier of an indefinitely large quantity of fat, provided that, in the splitting up of soap into fatty acid and alkali which occurs in the epithelial cells, the alkali makes its way, as is probable, back to the intestine, rather than into the blood-stream.

Histologists are unanimous that fat does not enter the epithelium in the particulate form of an emulsion; fat granules have never been observed in the striated border of these cells. Emulsification usually occurs, it is true, and this is obviously useful for the exposure of a large surface of fat to the action of the intestinal fluids; but fat absorption, as shown by the lacteals, proceeds alike whether any piece of gut contains emulsion or clear fluid. W. D. H.

The Fat of Flesh. By E. BOGDANOFF (*Pflüger's Archiv.*, 1896, **65**, 81—89).—Dormeyer's discovery (Abstr., 1895, ii, 540), that simple extraction of muscular tissue with ether is not sufficient to remove all the fat, is confirmed. By prolonged extraction with ether after the removal of the fat which is easily removable, a fat is obtained characterised, like butter fat, by a high percentage of volatile fatty acids. From the result of microscopical examination of the muscular tissue, which had been treated with osmic acid at different stages after ether extraction, the conclusion is drawn that the second fat is a constituent of the muscle-plasma. W. D. H.

Chemistry of Animal Fats. By CARL AMTHOR and JULIUS ZINK (*Zeit. anal. Chem.*, 1897, **36**, 1—17).—The authors, having special facilities for obtaining genuine specimens of the fat of various wild and domesticated animals, have made numerous estimations of specific gravity, melting and solidifying points, iodine and saponification numbers, both of the fats themselves and of the fatty acids, as well as the Hehner and Reichert values, the acetyl number (according to Benedikt and Ulzer), and the free acidity when fresh and after a lapse of time. The animals selected were the elk, red deer, fallow deer, chamois, roebuck, badger, wild boar, dog, fox, wild and domestic cat, pine marten, pole cat, hare, tame and wild rabbit, tame and wild duck and goose, and the last, after two years' captivity, domestic fowl, turkey, black cock, dove, and starling. The first five are distinguished from the others by high specific gravity and low iodine number, the iodine number of chamois fat being the lowest yet recorded. The fat of the wild boar, hare, wild rabbit, and black cock exhibits the property of drying to a varnish when exposed to the air in a thin layer; the fat of the domestic pig and rabbit does not dry. Comparing the fat of wild with that of domestic animals, the former always shows a higher iodine absorption and generally a higher acidity in the fresh state; in the case of the wild goose kept in captivity for two years, the iodine number had fallen to that of the domestic goose. Besides the above numerical values, observations of colour, consistency, odour, &c., are recorded. M. J. S.

Muscular Work and Glycogen. By FRIEDRICH SCHENCK (*Pflüger's Archiv.*, 1896, **65**, 326—328).—A further criticism of Seegen's work. (Comp Abstr., 1896, ii, 48). W. D. H.

Oxidation in the Tissues. By AN. MEDVEDEFF (*Pflüger's Archiv.*, 1896, **65**, 249—277).—The principal experiments recorded were made with salicylaldehyde and extracts of animal organs. Under certain circumstances, the amount of oxidation is proportional to the square of the concentration of the oxidation ferment (or active proteid), and inversely proportional to the square root of the concentration of the salicylaldehyde. Physiological oxidation processes belong to the class of what Schmiedeberg terms 'synthetic oxidations.' W. D. H.

Influence of Calcium Salts on Fibrin Formation. By OLOF HAMMARSTEN (*Zeit. physiol. Chem.*, 1896, **22**, 333—395).—A very complete and critical article on the recent theories that have been advanced concerning the part played by calcium salts in the process of blood-coagulation, the points of difference between the theorists being tested by carefully-devised experiments. The view of Alex. Schmidt, that calcium salts do not qualitatively act differently from other neutral salts like sodium chloride, is not correct. Schmidt admits that the calcium salts are quantitatively more active than other salts, but Arthus and Pagès are undoubtedly right in attributing to calcium salts a specific action; and the removal of such salts by the addition of alkali oxalates inhibits coagulation, because the plasma is thereby decalcified. The use of the term decalcification is not abso-

lutely correct, for the calcium which is in intimate union with fibrinogen is not influenced by the oxalate.

The question then arises what is the specific action of calcium salts? Are they of use in the formation of fibrin ferment, or do they act, as in the formation of casein in milk, by precipitating the proteid which has been subjected to the action of the ferment? The analogy drawn by Arthus between casein formation and fibrin formation only holds good in part, for calcium salts are not essential for the fermentative change of fibrinogen into fibrin; provided fibrin ferment is present in sufficient amount, fibrin is formed typically and abundantly from solutions of fibrinogen, whether calcium salts have been removed by an oxalate or not.

Pekelharing is right when he assumes that the specific action of calcium salts is in the genesis of fibrin ferment, or, to adopt a new nomenclature, in the change of prothrombin (zymogen or percursor of fibrin ferment) into thrombin (the ferment itself). Fibrin is certainly not a calcium compound of fibrinogen; both contain the same amount of calcium.

Lilienfeld's thrombin, a substance he considered he had split off from fibrinogen by the action of acids like acetic or nucleic acid, and which he further supposed combined with calcium to form fibrin, does not exist. It is nothing but fibrinogen itself partially precipitated by the acid employed. W. D. H.

NOTE BY ABSTRACTOR.—No reference is made in this paper to a preliminary note by E. A. Schäfer (*Proc. physiol. Soc.*, 1895, 18), who arrived at much the same results on most points. Ringer (*Practitioner*, **24**, 81) has also shown, in connection with cardiac muscle, that soluble oxalates do not produce absolute decalcification.

Fate of Cholesterol in the Animal Organism. By STANISLAS BONDZYŃSKI and V. HUMNICKI (*Zeit. physiol. Chem.*, 1896, **22**, 396—410).—In man, the cholesterol of the bile leaves the body in the fæces as a new substance *coprosterol*; this has the formula $C_{27}H_{48}O$, and from an examination of its derivatives (see this vol., i, 183), appears to be dihydrocholesterol. In dogs, cholesterol is found in the fæces as such. In horses, the material found is named *hippocoprosterol*, $C_{27}H_{54}O$, or $C_{27}H_{56}O$. W. D. H.

Behaviour of Formanilide in the Animal Organism. By FRIEDRICH KARL KLEINE (*Zeit. physiol. Chem.*, 1896, **22**, 327—332).—The urine of animals fed on a diet mixed with formanilide was examined; in dogs, small doses of the drug are almost entirely destroyed in the metabolic process; large doses lead to the appearance of orthohydroxycarbanil in the urine. This same substance was found by Jaffe after the administration of acetanilide. It is produced by oxidation and a subsequent loss of water,

$$C_6H_5\cdot NH\cdot COH + O_2 = OH\cdot C_6H_4\cdot NH\cdot COOH = C_6H_4{<}{\genfrac{}{}{0pt}{}{N}{O}}{>}C\cdot OH + H_2O.$$

In rabbits, the substance found in the urine is amidophenol. W. D. H.

Ingestion and Excretion of Iron in Health. By RALPH STOCKMAN and E. D. W. GREIG (*J. Physiol*, 1897, **21**, 55—57).—The iron meta-

bolism of the body, so far as regards intake and output, is extremely small, an examination of the ingesta and egesta in four series of observations made on three healthy adults showing in the first and fourth observations that the intake and output were almost equal, amounting to 6·2 and 6·3 milligrams in one case, and 3·5 and 3·7 milligrams in the other. In the other two series, the iron excreted on the three days of the analysis was much greater than the amount ingested, but at other times the balance must be reversed, or the equilibrium of health would not be maintained.

Concerning internal iron-metabolism, which must be considerable if blood corpuscles are broken down in such large numbers as is commonly supposed, little or nothing is known. The greater part of the iron is apparently not excreted, but retained in store by the liver for future use.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Alcoholic Fermentation without Yeast Cells. By EDUARD BUCHNER (*Ber.*, 1897, **30**, 117—124).—When brewery yeast, to which no starch has been added, is ground with quartz sand and kieselguhr, moistened with water and pressed, the liquid which is obtained has the power of producing the fermentation of sugar, although it appears to be quite free from yeast cells. It has a sp. gr. of 1·0416, contains about 10 per cent. of residue, and gelatinises when boiled. This liquid produces alcoholic fermentation in solutions of cane-sugar, maltose, glucose, and fructose, but does not ferment either lactose or mannitol. Fermentation continued in many cases for two weeks, even at the temperature of 0°, and was not stopped by filtration of the liquid through a Berkefeldt filter. Plate cultures showed that in some cases small numbers of micro-organisms were present, but yeast cells were in no case detected. The author gives the name *zymase* to the substance which produces the fermentation. This appears to be a proteid, since the fermentative power of the solution is practically destroyed when it is heated for an hour at 40—50° and the coagulated albumin filtered off. The dried precipitate produced by alcohol does not yield any ferment to water. A. H.

Effect of Ammonium Nitrate on Aspergillus niger. By CHARLES TANRET (*Compt. rend.*, 1896, **123**, 948—950).—When *Aspergillus niger* is sown in Raulin's solution, the spores germinate in less than 24 hours, forming a mycelium which soon produces black conidia. When, however, the ammonium nitrate in the nutrient solution is increased from 0·25 per cent. to 0·5 or 0·75 per cent., the spores, at a temperature of 30—40° produce a mycelium, which grows rapidly but does not fructify. At a temperature of 20—22°, even 1 gram of ammonium nitrate per 100 c.c. of solution does not prevent the formation of conidia. During the growth of the aspergillus in the mycelial state, both citric acid and nitric acid are formed in the solution, and

starch appears in the tissue of the mould. When grown in Raulin's solution, no starch is elaborated. A. C. C.

Behaviour of Bacteria towards Chemical Re-agents. By THEODOR PAUL and BERNHARD KRÖNIG (*Zeit. physikal. Chem.*, 1896, **21**, 414—450).—In order to determine quantitatively the effects of various acids, bases, oxidising agents, and metallic salts on bacteria, the numbers of colonies were counted after similarly-prepared cultivations were treated with the respective compounds. The bacteria employed in the experiments were *Staphylococcus pyogenes aureus*, and the spores of the anthrax germ, *Bacillus anthracis*, and numerous experiments were performed with each compound examined. The authors obtained the following results. The salts of mercury, gold, and silver exert a specific poisonous effect, strongest in the case of the mercury compounds; platinum salts have little action, if any. In metallic salt solutions in which the metal is present as a complex ion, the disinfecting action is extremely small; it is, however, not only dependent on the number of the metallic ions, but also on the anion and the non-dissociated part. The effect of mercuric chloride is greatly decreased by the addition of sodium chloride, or other chlorides, but is not affected by other salts, such as sodium nitrate. The acids only act as disinfectants in concentrations of the gram molecular weight per litre, and exhibit a specific action which is not proportional to the concentration of the hydrogen ions. The weak organic acids, however, appear to act according to the degree of dissociation. Lithium, sodium, and potassium hydroxides have almost equal effects, but the action of ammonium hydroxide is very slight. Of the oxidising agents, nitric acid, chromic acid, chloric acid, and permanganic acid act in the order stated, which is also that of their oxidising powers as determined electrically (Abstr., 1893, ii, 58). The halogens have also a specific action, which is most powerful in the case of chlorine. Phenol acts better in a 5 per cent. solution than at higher concentrations, and the effect is increased by the addition of metallic salts, most noticeably sodium chloride; it is, however, diminished by dissolution in alcohol, and in the most favourable conditions is not nearly as great as that of mercuric chloride, which appears to be the strongest disinfectant examined. In absolute alcohol, however, even this compound, like other salts, has little or no effect, but acts best in a solution containing water and alcohol in proportions which vary with the different compounds. L. M. J.

Chemistry of the Membranes of Lichens and of Fungi. By F. ESCOMBE (*Zeit. physiol. Chem.*, 1896, **22**, 288—306. Compare Winterstein, Abstr., 1894, ii, 425; 1895, i, 80, 199, 323, 493). The hyphen-membranes of *Cetraria islandica*, after the extraction of fats, oils, colouring matter, astringent substances, lichenin, &c., consists mainly of an insoluble anhydride of galactose, which the author terms *paragalactan*; on oxidation, it yields mucic acid. Lichenin on hydrolysis yields, apparently, only galactose (compare E. Fischer), and is, therefore, probably a galactan. No chitin, or related substance, and no cellulose could be detected. The membrane of *Peltigera canina* contains no cellulose, but apparently a small amount of chitin. *Evernia prunastre* was also investigated, the algæ cells contain cellulose, and the hyphen-membrane a substance which, on treatment with potassium

hydroxide, becomes gelatinous. A substance was obtained from the sclerotium of *Claviceps purpurea* which could not be identified.

J. J. S.

Crystalline Nitrogenous Compounds in Seedlings. By ERNST SCHULZE (*Zeit. physiol. Chem.*, 1896, **22**, 411—434. Compare Abstr., 1895, ii, 84).—Complete details for the isolation of the different amido-acids are given. Seedlings of *Picea excelsa*, grown in sand in a dark room, contain asparagine with a little glutamine, whilst in the open, in good soil, no asparagine, but a considerable amount of glutamine, can be obtained.

Etiolated seedlings of *Lupinus albus*, of $2\frac{1}{2}$ weeks' growth, yielded phenylalanine, amidovaleric acid, and asparagine, but apparently no leucine. Arginine could not be isolated from the cotyledons of the same seedlings. Normal green seedlings gave a quantity of leucine and amidovaleric acid, but only a little asparagine, and apparently no phenylalanine. Green seedlings of *Lupinus luteus* gave leucine, a small quantity of asparagine, and a fair amount of arganine.

Etiolated seedlings of *Lupinus angustifolius L.* yielded leucine and amidovaleric acid, and the presence of small quantities of phenylalanine and arginine was also indicated.

J. J. S.

Nitrogenous Compounds derived from the Proteid Substances of certain Conifers. By ERNST SCHULZE (*Zeit. physiol. Chem.*, 1896, **22**, 435—448. Compare Abstr., 1895, ii, 84).—Etiolated seedlings of *Picea excelsa* contain arginine, together with smaller quantities of asparagine and glutamine; normal green seedlings, however, contain arginine and glutamine, but no asparagine. The seedlings of *Abies pectinata* contain even more arginine, but little or no glutamine and asparagine. Seedlings of *Pinus sylvestris* contain arginine and asparagine, with a little glutamine.

J. J. S.

Analyses of the Juice of Different Varieties of Gooseberries, Currants, and Strawberries. By ALBERT EINECKE (*Landw. Versuchs.-Stat.*, 1896, **48**, 131—160. Compare Abstr., 1895, ii, 366.)—The analyses include invert and cane-sugar, acid, extract, nitrogenous matter, crude ash, phosphoric acid, and potash. The sp. gr. of the juice was also determined. The results are given in percentages in the berries.

The variations in the amounts of important constituents in the different varieties are, as a rule, not considerable, and it is not at present possible to ascertain by analysis to what variety a sample belongs. Comparing the produce of 1894 and of the dry season of 1895, it was found that, whilst gooseberries were richer in juice in 1894, the currants contained more juice in 1895. The juice of both fruits was richer in constituents in 1895 than in 1894 (except nitrogen in currants). With regard to the influence of manures on the composition of the juice, no effect was observed in the case of gooseberries and currants. In the case of strawberries, there was an increase of valuable constituents under the influence of manure, whilst the percentage of nitrogen was lowered; of ash constituents the amount of potash was increased, whilst that of phosphoric acid was diminished, by manuring.

N. H. J. M.

Analytical Chemistry.

Estimation of Sulphur in the Gases Produced by the Combustion of Petroleum. By RICHARD KISSLING (*Chem. Zeit.*, 1896, **20**, 199).—A small lamp, with a reservoir capable of holding about 100 grams of oil, is fitted with a lamp-glass made of hardened glass the top of which is drawn out and bent so that it may be connected with a series of absorbing tubes.

By means of a current of air, the products of combustion are first passed through a U-tube 200 mm. long filled with glass beads moistened with a 5 per cent. solution of potassium permanganate. The gases then again pass through a nitrogen bulb also filled with permanganate solution, and finally through an empty bulb. When the combustion is over, the tubes are rinsed, the liquid cleared by boiling with hydrochloric acid, and the sulphuric acid estimated with barium chloride in the usual manner. The air in the room should, of course, be free from any sulphurous vapours. L. DE K.

Estimation of Ammoniacal Nitrogen in Artificial Manures. By O. BÖTTCHER (*Chem. Zeit.*, 1896, **20**, 151—152).—The author has proved by a large number of experiments that ammoniacal salts contained in manures are completely decomposed by boiling with water and calcined magnesia. Boiling with aqueous soda is, therefore, unnecessary, and is often the cause of finding too high a percentage of ammonia, due to decomposition of the nitrogenous organic matter.

The magnesia should, however, be free from carbonate—if not, the results will be untrustworthy. L. DE K.

A New Method of Estimating Phosphorus in Phosphor-Bronze. By FELIX OETTEL (*Chem. Zeit.*, 1896, **20**, 19—20).—From 3 to 10 grams of the sample in turnings or filings is digested with nitric acid, and the oxide of tin collected, slightly washed, dried, and ignited in a porcelain crucible; it is then mixed with about thrice its weight of potassium cyanide and fused for a few minutes at a red heat. In this way, the oxide is reduced to metallic tin, and the melt contains, besides potassium cyanide and cyanate, all the phosphorus as potassium phosphate. The melt is boiled with water, filtered, the cyanogen compounds removed by boiling with hydrochloric acid, and the traces of tin or copper which have again passed into solution are precipitated by a current of hydrogen sulphide and the whole filtered. The filtrate is concentrated to a small bulk, the last traces of the hydrogen sulphide are decomposed by adding a little bromine water, and the phosphoric acid is finally precipitated by adding ammonia magnesium mixture. The test-analyses are satisfactory; the presence of arsenic does not interfere. L. DE K.

Critical Examination of Methods for the Estimation of Phosphoric Acid. By C. MEINEKE (*Chem. Zeit.*, 1896, **20**, 108—113). —The author has long ago proposed to ignite the yellow phosphomolybdate precipitate before weighing it; the latest investigation shows that it contains 3·944 per cent. of phosphoric anhydride.

The precipitation of phosphoric acid by means of molybdate solu-

tion is not influenced by the presence of an excess of ammonium chloride.

The magnesium pyrophosphate obtained when the magnesium method of precipitating phosphoric acid is employed, is not the stable compound which it was formerly believed to be, but contains what may be regarded as free phosphoric acid, which volatilises at a very high temperature. The author thinks the precipitate should be first ignited in the ordinary way and then at a much stronger heat; the loss then observed represents the free acid. L. DE K.

Estimation of Phosphorus in Coal Ash. By LOUIS CAMPREDON (*Compt. rend.*, 1896, **123**, 1000—1003).—When very finely-powdered coal-ash is heated with concentrated hydrochloric acid for 15 or 20 hours, the whole of the phosphorus does not dissolve, and the proportion that remains in the residue is greater the higher the temperature to which the ash has been heated. It often amounts to 10 per cent., and may amount to as much as 25 per cent. of the total phosphorus present.

In order to get the whole of the phosphorus into solution, the ash must be heated with five times its weight of a mixture of equal parts of potassium and sodium carbonates. C. H. B.

Estimation of Readily-Soluble Phosphoric Acid in Basic Slags. By MAX GERLACH and MAX PASSON (*Chem. Zeit.*, 1896, **20**, 87—88).—The authors have shown that the active ingredient of Wagner's solution is the free citric acid, and that the large amount of ammonium citrate may be safely reduced to one-tenth. At a temperature of 17·5°, a 3 hours' treatment does not yield more soluble phosphoric acid than half-an-hour's extraction. This does not, however, imply that the undissolved phosphate is really insoluble; treatment with fresh quantities of solution will gradually dissolve it completely.

L. DE K.

Phosphoric Acid: Estimation of Pyrophosphoric Acid. By MARCELLIN P. E. BERTHELOT and GUSTAVE ANDRÉ (*Compt. rend.*, 1896, **123**, 773—776).—The method described is available in presence of orthophosphoric acid, but is not generally applicable in presence of metaphosphoric acid. The solution is precipitated with a mixture of magnesium chloride and ammonium chloride and acetate in presence of a considerable excess of acetic acid, and the liquid is heated on a water bath for 3 to 4 hours, in order to ensure complete precipitation. The pyrophosphate thus obtained contains a somewhat variable proportion of magnesium, and therefore it is washed, dissolved in dilute nitric acid, boiled for about an hour, and the orthophosphate into which it is converted is then precipitated in the usual way.

The magnesium pyrophosphate is comparatively stable, even when boiled with dilute acetic acid, but it is obvious that the boiling should not be too prolonged.

When orthophosphoric acid is also present, the filtrate from the precipitated pyrophosphate is concentrated and mixed with ammonia, which precipitates the phosphoric acid in the usual form.

C. H. B.

Volumetric Estimation of Arsenic. By Emerich Szarvasy (*Ber.*, 1896, **29**, 2900—2902).—The arsenic is precipitated in the usual way as sulphide, the precipitate being collected by filtration through a plug of asbestos placed in a combustion tube. After being washed with alcohol and ether, and carefully dried in a current of warm air, it is heated in a stream of oxygen. The arsenious anhydride which condenses in the cold part of the tube is dissolved in aqueous soda, and estimated by means of iodine solution. A. H.

Volumetric Estimation of Boric Acid. By Max Hönig and Gustav Spitz (*Zeit. angw. Chem.*, 1896, 549—552).—The authors titrate the free acid with standard alkali in the presence of a sufficiency of glycerol, using phenolphthalein as indicator. As soon as the liquid turns red, more glycerol is added, and should this destroy the colour, more soda is run in. When dealing with borates or mixtures of the same with alkali carbonates, a little methyl-orange is first added and then a slight excess of hydrochloric acid. After boiling, using a reflux condenser, the liquid is cooled, carefully neutralised, and the boric acid estimated as directed above. Insoluble borates are boiled with excess of normal acid and then treated in the same way.

When the acid has to be estimated in the presence of silica—for instance, in enamels—the sample is fused with potassium sodium carbonate, the melt boiled with water, and the liquid mixed with ammonium chloride in quantity sufficient to nearly neutralise the alkali used. After boiling for some time, an ammoniacal solution of zinc oxide is added to complete the precipitation of the silica, and when the ammonia has been entirely driven off, the liquid is filtered and the precipitate washed with hot water. A drop of methyl-orange is next added to the filtrate, then a slight excess of normal hydrochloric acid, and after boiling the mixture is treated as before.

Another process worked out by the authors is based on the following principles. Native insoluble borates, when made into an impalpable powder, are completely decomposed by boiling with solution of sodium hydrogen carbonate, passing carbonic anhydride through the boiling liquid. The solution, which then contains sodium tetraborate, and, of course, also alkali carbonate, is mixed with ammonium nitrate, and the carbonic acid quantitatively precipitated by silver nitrate, without throwing down any boric acid. When the liquid is now mixed with excess of ammonium chloride and distilled in a current of steam, the distillate contains an amount of free ammonia equivalent to the sodium in the tetraborate. From the amount of soda, the quantity of boric acid can readily be calculated. The results obtained by the second method agree fairly well with those obtained by the first process.

L. de K.

[Note by Abstractor.]—The titration of boric acid by means of glycerol, alkali, and phenolphthalein has been described by Thomson (Abstr., 1894, ii, 28); 30 per cent. of glycerol by volume was found to be always sufficient.

Estimation of Sodium Carbonate, Silicate, and Borate in Soap. By Wm. Waltke (*Chem. Zeit.*, 1896, **20**, 20—21).—From

5 to 10 grams of the soap, previously cut up small, is treated with boiling alcohol, and the insoluble portion is dissolved in hot water, filtered, evaporated to dryness, and the residue dried until the weight is constant. In an aliquot part of this residue, the carbonic anhydride is estimated in a Geissler's apparatus, and from the result the amount of sodium carbonate is calculated. The remainder is then treated with hydrochloric acid and the silica separated in the usual manner; in the filtrate from the silica, the whole of the sodium is present as chloride. This is now estimated volumetrically, and from the total thus found, the amount corresponding with the silicate and carbonate of sodium is subtracted; from the difference, the amount of sodium present as borate can be calculated.

When the salts are present in fair proportions, the results obtained by the process are quite satisfactory. L. DE K.

New Method of Estimating Potassium. By PAUL LÖSCHE (*Chem. Zeit.*, 1896, **20**, 38—39. Reply by H. HAEFCKE, *ibid.*, 88—89).—This process is intended for the analysis of crude potassium compounds containing an approximately known amount of potassium. Fifty grams of the sample is boiled with 150 c.c. of water and 10 c.c. of strong hydrochloric acid, and, when cold, diluted to 200 c.c.; 10 c.c. of the filtrate is then mixed with a sufficiency of platinic chloride solution, evaporated to dryness, and the residue broken up and repeatedly extracted with 96 per cent. alcohol to remove any sodium platinochloride. The insoluble matter is collected on a weighed filter, dried at 120°, and then washed with a 10 per cent. solution of ammonium chloride at 30° to remove the sulphates; the ammonium chloride in turn is removed from the insoluble residue of potassium platinochloride by washing with alcohol, and the filter and constants dried at 120—130°. The test-analyses are satisfactory.

HAEFCKE sharply criticises the process, and does not hesitate to reject the method as being quite untrustworthy. L. DE K.

Estimation of Potassium at the Stassfurt Works. By ALBERT ATTERBERG (*Chem. Zeit.*, 1896, **20**, 131. By RUDOLF RUER, *ibid.*, 270, and by EMIL BAUER, *ibid.*, 270).—ATTERBERG states that the chemists at the Stassfurt potash works use a process which gives results sometimes 2 per cent. in excess of the truth, and attributes this to the incomplete washing of the precipitated platinochloride. This should not be put on to the filter until completely exhausted with alcohol in the dish, and should be well broken up with a glass rod.

RUER also complains about the process giving results which are too high, amounting to about $\frac{1}{2}$ a per cent., and proposes to lower the factor 0·3056 to 0·304 so as to counterbalance the error.

BAUER prefers to avoid the weighing on a filter, and to redissolve the precipitate in boiling water. The liquid is then evaporated in a weighed platinum dish, and the residue dried at 120°. L. DE K.

Estimation of Potassium at the Works at Leopoldshall, Stassfurt. By TIETJENS and APEL (*Chem. Zeit.*, 1896, **20**, 202—203).—The authors, in reply to Atterberg (preceding abstracts), suggest

that the difference in the percentage of potassium found may possibly be due to the samples having absorbed moisture. L. DE K.

E imation of Potassium as Potassium Platinochloride. By HEI ICH PRECHT (*Chem. Zeit.*, 1896, **20**, 209).—A reply to Atterberg (prec ding abstracts). The author recommends treating the platinochloride residue with commercial absolute alcohol instead of spirits of wine; contrary to theory, the sodium platinochloride is more readily soluble in the former liquid, whilst the potassium salt is practically insoluble. L. DE K.

Analysis of Commercial Copper by Electrolysis. By A. HOLLARD (*Compt. rend.*, 1896, **123**, 1003—1005).—Ten grams of the copper is placed in water and 15 c.c. of concentrated sulphuric acid, and 40 c.c. of nitric acid of 36° B is added. Towards the close of the reaction, the liquid is gently heated. Antimony sometimes separates, but, if the quantity is small, it does not interfere with the estimation of the copper; if large, it is separated by filtration, dissolved in aqua regia containing a high proportion of nitric acid, evaporated to dryness, dissolved in dilute hydrochloric acid containing tartaric acid, and added subsequently to the liquid from which the copper has been removed, and in which the antimony is to be estimated.

The copper solution is diluted to about 350 c.c., Luckow's electrodes (cone and spiral) are introduced, the base of the spiral being about 6 mm. below the base of the cone, which should be completely covered by the liquid, and a current of about 0·3 ampère is allowed to pass until all the copper is precipitated. The firmly adherent deposit on the cone contains the copper and the silver. Part, but not all, of any lead that may be present will be deposited on the spiral as peroxide.

When more or less than 10 grams of copper is taken, the best quantities of sulphuric and nitric acid respectively are, for 1 gram, 1 c.c. and 30 c.c.; for 3 grams, 6 c.c. and 33 c.c.; for 5 grams, 10 c.c. and 35 c.c.; for 20 grams, 20 c.c. and 60 c.c.

The estimations of the other constituents of the copper will be described subsequently. C. H. B.

Nessler's Reaction as a Test for Mercury or Iodides. By GEORGES DENIGÈS (*Chem. Zeit.*, 1896, **20**, 70).—*Detection of Mercury.* The solution, measuring about 2 c.c., is mixed with 2 c.c. of ammonia, and potassium iodide is added in quantity just sufficient to redissolve the precipitate. On adding aqueous potash, the characteristic brown colour will appear.

Detection of Iodine.—The solution is, if necessary, precipitated with ammonium sulphide, and the filtrate boiled to expel the excess of the reagent. Ammonia and aqueous soda are first added to it, and then a solution of mercuric chloride, when the well-known coloration will be produced. L. DE K.

Estimation of Mercury Salts by means of Sodium Dioxide. By M. C. SCHUYTEN (*Chem. Zeit.*, 1896, **20**, 239).—The process is based on the remarkable fact that sodium dioxide, which possesses such strong oxidising properties, is yet capable of reducing mercury compounds to the metallic state.

The mercury compound, soluble or insoluble, is mixed with a sufficiency of water contained in a porcelain basin fitted with an inverted funnel, the stem of which is bent at right angles. Sodium dioxide is introduced in small portions at a time, as long as a precipitate is formed and after putting on the funnel the whole is gently heated until vapours begin to condense in the neck of the funnel. When cold, the funnel is rinsed, and the metallic mercury is collected on a weighed filter, and dried in a desiccator. The process is not applicable to the native sulphide. L. DE K.

Estimation of Thorium in Thorite. By ERNST HINTZ and HERMANN WEBER (*Zeit. anal. Chem.*, 1897, **36**, 27—31).—The separation of thoria from the oxides of the cerium and yttrium metals is based on the solubility of thorium oxalate in ammonium oxalate, and its reprecipitation from this solution on the addition of hydrochloric acid. In opposition to Glaser (*Chem. Zeit.*, 1896, **20**, 613), the authors find that thorium oxalate dissolved in a hot concentrated solution of ammonium oxalate is not precipitated on diluting and cooling. The hydrochloric acid solution of 1 gram of the substance, freed from silica by evaporation, and from heavy metals by hydrogen sulphide, is diluted to 200 c.c. and precipitated hot by 1 gram of oxalic acid. After remaining for two days, the precipitate is collected, washed, and digested for several hours on the water bath with 60 c.c. of a solution (saturated cold) of ammonium oxalate. The mixture is diluted to 300 c.c., and allowed to remain cold for two days, then filtered, and the filtrate heated with 5 c.c. of concentrated hydrochloric acid, whereby the thorium oxalate is completely precipitated. The residue left undissolved by the ammonium oxalate is repeatedly digested with fresh portions of oxalate solution, and the filtrates treated as before. The thorium oxalate is then washed and ignited. It is, however, not yet quite free from cerium and yttrium. It is therefore redissolved, either by boiling with hydrochloric acid or by fusion with potassium hydrogen sulphate, precipitated with ammonia, dissolved in hydrochloric acid, and, after evaporation to expel excess of acid, its feebly acidified solution (diluted to 300 c.c.) is boiled with 3—4 grams of thiosulphate. The filtrate is precipitated by ammonia, the washed precipitate dissolved in hydrochloric acid, the solution evaporated, then taken up with a little water, and the boiling solution treated with a hot concentrated solution of ammonium oxalate. Water is added, and the mixture allowed to remain long in the cold. The precipitate consists of the oxalates of the cerium and yttrium metals, and the weight of the oxides is deducted from that of the impure thoria.

In some cases of very impure thorites, it is necessary to ignite the oxalates left undissolved by ammonium oxalate, and, after bringing them into solution as chlorides in feebly acidified water, to apply the thiosulphate method for the precipitation of the thoria present; but as the precipitation of thoria by this means is imperfect, the filtrate also requires to be treated by the ammonium oxalate separation method. (Compare Abstr., 1896, ii, 677.) M. J. S.

Use of Nitroso-β-Naphthol in Inorganic Analysis. By ROBERT BURGASS (*Zeit. angw. Chem.*, 1896, 596—601).—This reagent, first intro-

duced by von Knorre for the separation of cobalt and nickel (Abstr., 1893, ii, 500), has been tried by the author for the separation of other metals. He finds that copper, cobalt, and iron are completely precipitated; silver, tin, bismuth but partially, and these should, therefore, be removed before adding the nitrosonaphthol. Mercury, nickel, chromium, manganese, lead, zinc, aluminium, cadmium, magnesium, calcium, beryllium, antimony, and arsenic remain in solution.

In presence of excess of iron, any phosphoric acid will also be carried down; molybdic or titanic acid interferes with the accurate estimation of the cobalt or copper. L. DE K.

Assay of Chrome Yellow and Chrome Red. By HUGO AMSEL (*Zeit. angw. Chem.*, 1896, 613—618).—The author thinks that, if the sample is free from the carbonates and sulphates of barium, calcium, and lead, it may be passed as commercially pure. If a quantitative analysis has to be made, the best plan is to boil about 0·5 gram of the compound with a 10 per cent. solution of aqueous potash for some time; hydrochloric or nitric acid is then added in slight excess, and any insoluble matter, such as barium sulphate, is collected and weighed.

The filtrate is mixed with excess of sodium carbonate, and heated, with addition of bromine; the precipitate contains calcium carbonate and lead carbonate (the latter being partially converted into dioxide), whilst the filtrate contains sodium chromate and sulphate. The details present no novel features. L. DE K.

Separation of Tungsten and Titanium. By ED. DEFACQZ (*Compt. rend.*, 1896, **123**, 823—824).—A mixture of 8 parts of potassium nitrate and 2 parts of potassium carbonate, heated at its melting point, completely dissolves tungstic anhydride in 8 or 10 minutes, whether the anhydride has previously been strongly heated or not. Metallic tungsten is likewise dissolved. On the other hand, the fused mixture does not dissolve either titanium oxide or metallic titanium.

The substance to be analysed is heated to dull redness for 20 to 30 minutes with 7 to 8 times its weight of the mixture of nitrate and carbonate specified, and, after cooling, the product is treated with water and evaporated to dryness. The residue is first extracted with water and then washed with water containing ammonium nitrate, in order to prevent the titanium oxide from passing through the filter. The insoluble residue is dried, strongly heated, and afterwards fused with potassium hydrogen sulphate, the titanium being estimated in the usual way.

The tungsten in the solution is precipitated as mercurous tungstate. C. H. B.

Commercial Prussian Blue. By ERNEST J. PARRY and JOHN HENRY COSTE (*Analyst*, 1896, **21**, 225—230).—The authors have examined a large number of samples of commercial Prussian blue, and tabulated the results.

The chief point in the analysis is the estimation of the total iron, and the nitrogen; the latter by Kjeldahl's process. The factors for converting these into Prussian blue are respectively 3·03 and 4·4. In properly manufactured samples, the results obtained from these estimations ought to agree, but there may be occasionally either excess of iron or of nitrogen in the form of alkali or even of aluminium

ferrocyanide. Commercial blue may be passed as sufficiently pure if it contains 30 per cent of total iron and 20 per cent. of nitrogen. When boiled with sulphuric acid, it should become colourless in a few minutes without any charring. L. DE K.

Analysis of "Cap Composition." By F. W. JONES and F. A. WILLCOX (*Chem. News*, 1896, **74**, 283).—The method is based on the solubility of mercury fulminate in acetone saturated with gaseous ammonia. A tared filter paper is placed in a funnel to the neck of which has been fitted a piece of rubber tubing provided with a clip. The paper is moistened with a solution of ammonia in acetone; the finely-powdered cap composition is weighed off directly on to the filter paper, covered with the solution of ammonia in acetone, and the whole allowed to remain for 3 or 4 hours. It is then washed repeatedly with the same solution until the washings give no coloration with ammonium sulphide, and afterwards washed with acetone until the washings give no residue on evaporation; it is then dried, and weighed; the loss gives the amount of mercury fulminate. The paper and contents are again put in the funnel, washed with water until free from potassium chlorate, dried, and weighed; the further loss in weight gives the amount of potassium chlorate, and by deducting the weight of the filter paper from the last weighing, the amount of the antimony sulphide is obtained. D. A. L.

Molybdic Acid, a Reagent for Alcohol. By C. EMANUEL MERCK (*Chem. Zeit.*, 1896, **20**, 228).—By means of molybdic acid, it is possible to detect the presence of 0·2 per cent. of methylic alcohol, or 0·02 per cent. of ethylic alcohol, in the absence, of course, of any organic matter capable of interfering with the test. This is best carried out by dissolving molybdic acid in sulphuric acid at 60°, and pouring the hot solution gently into the liquid to be tested, when a blue ring will form at the surface of contact. On shaking, the colour disappears, but returns on adding more of the reagent.

L. DE K.

Estimation of Alcohol by Means of the Ebullioscope; Influence of Extractive Matters. By FRANZ FREYER (*Zeit. angw. Chem.*, 1896, 654—659).—The principle of the instrument (of which there are several varieties) is based on the difference between the boiling point of pure water and that of the spirit to be tested; a table is then referred to for the alcoholic strength of the sample.

The author points out that in the presence of much extractive matter the results are untrustworthy, as the alcohol may then be found several per cents. too high. A new table allowing for extractive matter is given. L. DE K.

Detection of Caramel in Wine, and its Possible Confusion with Coal-tar Colours. By A. J. DA CRUZ MAGALHAËS (*Compt. rend.*, 1896, **123**, 896—897).—A sample of port wine examined by the author gave reactions pointing to the presence of a coal-tar colouring matter, although it was known that only caramel made from cane-sugar had been added. Further exeriments showed that caramel prepared from cane-sugar differs considerably from caramel made from

glucose, in that it behaves with certain reagents exactly like a coal-tar colour. Thus, when treated with basic lead acetate and then shaken with amylic alcohol, the former caramel communicated an orange-yellow colour to the solvent, whilst with the glucose caramel no coloration occurred. Ether, when shaken with a solution of the former, acquired an orange yellow colour, whilst with the latter no colour was extracted. Mordanted wool was dyed orange by the former, yellow by the latter. Genuine wine, to which no caramel had been added, did not give these reactions. A. C. C.

Simple and Convenient Extraction Apparatus for the Analysis of Food Stuffs. By J. L. Beeson (*J. Amer. Chem. Soc.*, 1896, **18**, 744—745).—A modification of the Johnston extractor. The extraction tube, which is rather short, has a funnel stopper, and is so constructed that the sample may be weighed and dried in the same before extraction. After placing the tube in a Stutzer tube, the extraction with ether, &c., proceeds as usual, the returning drops of liquid being allowed to fall through the funnel tube on to the centre of the sample, so as to avoid loss of the latter. L. de K.

Reformation of the Present Methods of Analysis of Food Stuffs. By F. Josef König (*Landw. Versuchs.-Stat.*, 1896, **48**, 81—110). —Owing to the probable difference in nutritive value of the pentosans and hexosans, it is desirable, if possible, to estimate separately the amounts of these two groups in food stuffs.

Experiments were first made in which rye grain and straw, and pea corn and straw, were treated with 1·25 per cent. sulphuric acid and 1·25 per cent. caustic potash. Both solutions dissolved more or less of the pentosans, and even 0·3 per cent. potash dissolved some, but in no case was the solution complete.

Superheated water dissolved the pentosans in rye flour and straw almost completely as well as the starch. When, therefore, starch is estimated by first dissolving with superheated water and subsequent inversion, results are obtained which are more or less too high, since the dissolved pentosans reduce Fehling's solution as well as the hexoses. To obtain more correct results for starch, it is therefore proposed (when superheated water is employed) to ferment the inverted solution with beer-yeast, and to estimate the carbonic anhydride or the alcohol produced. The method is, however, not perfect, owing to the production of hexoses from the cell-membrane. Pentosans seem to accompany the hexosans in all parts of plants. The following amounts of pentosans were found in starch from different sources: potato-starch, 1·25; maize-starch, 2·04; rice-starch, 1·40, and wheat-starch, 1·05 per cent.

Estimation of starch as maltose after treatment with diastase gave results which were too high, although less of the pentosans was dissolved than when superheated water was employed. The fermentation method would give better results.

The usual process of food stuff analysis has two faults, the use of too dilute acid and the use of too strong alkali. The acid is not strong enough to dissolve all the hemicellulose, whilst the alkali dissolves, besides fat and proteids, lignin, which should be either determined along with cellulose or else separately. With regard to alkali, it was

found that 0·5 per cent. soda solution dissolved almost the whole of the nitrogenous matter of the food, leaving a residue of crude fibre containing much the same amount of nitrogen as when 1·25 per cent. potash was used. The use of the more dilute alkali has the advantage that the lignin present is less attacked, and may therefore be estimated separately.

Experiments with different strengths of acid are still in progress, but the results so far obtained indicate that, whilst less than 12 per cent. hydrochloric acid is insufficient to dissolve the whole of the pentosans, better results may be obtained by heating under pressure with more dilute acid. N. H. J. M.

Formaldehyde as a Reducing Agent. Estimation of Formaldehyde. By BRUNO GRÜTZNER (*Arch. Pharm.*, 1896, **234**, 634—640).—To estimate potassium chlorate, the aqueous solution (about 2 per cent.) may be mixed with formalin (35 per cent. aqueous solution of formaldehyde—5 grams) nitric acid (5 c.c.; strength not named) and excess of silver nitrate solution. The mixture is heated on the water bath for half-an-hour, and the precipitated silver chloride then estimated by any of the usual methods.

Potassium bromate may be estimated on precisely similar lines, save that the heating must be continued for 2—2½ hours in order to complete the action. Iodates are not reduced by this method, and perchlorates only partially; periodates are reduced to iodates.

By mixing a measured volume of a formalin solution with an excess of potassium chlorate, adding a measured excess of N/10 silver nitrate solution, heating the mixture in the water bath until further heating produces no turbidity in the clear liquid above the settled precipitate, and titrating the excess of silver nitrate solution with potassium thiocyanate in the usual manner, the strength of the formalin solution may be determined. One molecule of silver nitrate corresponds with three of formaldehyde. A. G. B.

Estimation of Formaldehyde. By GYSBERT ROMIJN (*Zeit. anal. Chem.*, 1897, **36**, 18—24).—Besides reviewing the methods of Legler (Abstr., 1883, 1035) and of Brochet and Cambier (Abstr., 1895, i, 325) the author proposes two new ones, the first depending on oxidation by iodine in alkaline solution, and the second on the combination of formaldehyde with potassium cyanide, and he has studied their suitability for estimating formaldehyde both when occurring alone and when mixed with other substances of an aldehydic character, such as acetaldehyde, acetone, and benzaldehyde. A solution of formalin was used for the experiments. With the pure substance, all four methods gave practically identical results (37·38—37·9 per cent.), but owing to the want of sensitiveness of litmus in solutions containing hexamethylenetetramine, Legler's method requires the use of much stronger solutions than the other three, and is altogether of inferior accuracy.

The operations in the new methods are as follows. To a quantity of the solution containing about 15 milligrams of formaldehyde, there is added 25 c.c. of a N/10 iodine solution, and so much strong soda solution that the mixture becomes pale yellow. After 10 minutes, a small excess of hydrochloric acid is added, and the free iodine is titrated

with thiosulphate. Two atoms of iodine are consumed by 1 molecule of formaldehyde. With the pure substance, the results are perfectly concordant, and the great convenience of the method renders it the most advantageous of the four. It cannot, however, be used in the presence of the other aldehydes, and in the case of acetone, which, as shown by Krämer and Messinger, forms iodoform with quantitative completeness, the two substances are estimated jointly.

The reaction with potassium cyanide consists in the combination of the two substances in molecular proportion. Somewhat more than this amount of cyanide (in a solution containing about 6 grams per litre) is therefore added, and the mixture is poured into an excess of a N/10 solution of silver nitrate containing so much free nitric acid that the mixture remains acid. The excess of cyanide separates as silver cyanide, and the unprecipitated silver is titrated with ammonium thiocyanate (Volhard's process). In the presence of acetaldehyde, the aldehydecyanide mixture must be immediately added to the silver nitrate or the results obtained will be too high, but acetone and benzaldehyde are without influence, even if half-an-hour elapses at this stage. Legler's method seems not to be affected by the presence of the above three foreign substances, but the hydroxylamine method cannot be used in presence of any of them. M. J. S.

Polarimetric Estimation of Tartaric Acid. By ALBERT COLSON (*Bull. Chim. Soc.* [3], **15**, 158).—The author experimented with solutions of tartaric acid of different strengths, made just alkaline with ethylenediamine. In the absence of impurities, and for solutions containing not more than 100 grams of tartaric acid per litre, the concentration could be directly determined from the observed rotation. In the presence of a substance such as citric acid, it was found that an error was introduced which increased with the amount of the second substance present. The observations could, however, be corrected by means of an empirical equation involving the density of a solution containing the same amount of ethylenediamine tartarate, and the density of the solution under observation. M. W. T.

Estimation of Fat in Milk. By HEINRICH FRESENIUS (*Zeit. anal. Chem.*, 1897, **36**, 31—32).—The author, having made numerous comparisons of the methods of Gerber and Babcock (Abstr., 1891, 508) with the gravimetric process of extracting the milk, previously dried on sand, by ether, and weighing the residue obtained from the ethereal extract, finds that the results of the three methods agree satisfactorily. Gerber's process consists in mixing 10 c.c. of sulphuric acid (sp. gr. 1·82—1·83) with 1 c.c. of amylic alcohol and adding 11 c.c. of the milk. The flask is then closed by a caoutchouc stopper, well shaken, and then revolved for 3 minutes in Gerber's centrifugal machine. The fat collects in a graduated portion of the special-shaped vessel, and the reading gives the percentage at once. M. J. S.

Method of Establishing the Purity of Butter by Determining the Specific Gravity. By RAOUL BRULLÉ (*Bied. Centr.*, 1896, **25**, 638; from *Milchzeit.*, 1896, 297, and *Journ. Agric.*, 7 March, 1896).—The failure of sp. gr. determinations of butter fat as a means

of ascertaining the purity of butter, is attributed to the presence o water, colouring matter, &c. The following method is recommended for obtaining the fat in a pure state. The butter (100—500 grams) is melted, the fat separated as far as possible, violently shaken for some minutes with finely powdered calcium chloride (5—6 per cent.) and powdered animal charcoal (4 per cent.), and filtered. The fat, which is now colourless and quite dry, has a sp. gr. of 0·8655 at 100°, whilst oleomargarin has a sp. gr. = 0·8600, and the addition of 10 per cent. of margarin lowers the sp. gr. of butter fat by 0·00055.

N. H. J. M.

Separation of Trimethylamine from Ammonia. By HERMANN FLECK (*J. Amer. Chem. Soc.*, 1896, **18**, 670—672).—The mixed hydrochlorides are repeatedly extracted with boiling absolute alcohol, which is then distilled off in a 750 c.c. distilling flask. Excess of aqueous soda is added to the residue, and the gases given off on boiling are passed into a large volume of water; litmus is added, and the liquid is neutralised exactly with dilute sulphuric acid. The whole is now evaporated to dryness, and the residue extracted with 1 litre of cold, absolute alcohol, which dissolves the trimethylamine sulphate, leaving the ammonium compound undissolved. The alcohol is distilled off, and the residue transferred to a weighed dish and dried until the weight is constant.

L. DE K.

Colour Reactions of Brucine; Detection of Nitrites in Presence of Sulphites. By P. PICHARD (*Compt. rend.*, 1896, **123**, 590—592).—Brucine in presence of hydrochloric acid and a trace of a nitrite yields, in 5 minutes or less, a vermilion red coloration which changes to pale yellow; this reaction is capable of detecting 1 part of nitrous acid in 640,000 parts of water. A nitrate under the same conditions gives no coloration. Chlorine and hypochlorous acid give no coloration with free brucine, but an intense vermilion coloration with the nitrate, chloride, acetate, and sulphate, especially the latter.

The presence of sulphites or sulphurous acid very materially reduces the sensitiveness and accuracy of the ordinary reactions for the detection and estimation of nitrous acid, and hence they cannot well be applied to soils which have been treated with calcium sulphate, and may in consequence contain lower sulphur compounds; this applies also, of course, to water that has percolated through such soils. On the other hand, the presence of 1 part of sulphurous acid in 2060 parts of water reduces the sensitiveness of the brucine test only to one-half, so that 1 part of nitrous acid in 329,000 parts of water can still be detected. This reaction should be used for the detection of nitrites in soils or drainage waters which may also contain sulphites. In either case, sulphides must first be removed if they are present; this is best done by agitating the solution with finely divided lead sulphate.

C. H. B.

Testing Quinine Sulphate. By MELCHIOR KUBLI (*Arch. Pharm.*, 1896, **234**, 570—585).—A reply to O. Hesse (Abstr., 1896, ii, 550).

A. G. B.

General and Physical Chemistry.

Optical Activity of Aspartic Acid in Aqueous Solutions. By ELLEN P. COOK (*Ber.*, 1897, **30**, 294—297).—It is well known that aspartic acid is dextrorotatory in all solutions to which acids have been added, but lævorotatory in those which contain alkalis. Investigators, however, differ as to the rotation of aqueous solutions of the pure acid. The author finds that a solution of the acid containing 1·872 parts of aspartic acid in 100 is dextrorotatory below 75°, but lævorotatory above that temperature. The addition of a single drop of aqueous caustic soda renders the solution lævorotatory, even at 20°.

The following are the values obtained.

Grams of Aspartic Acid in 100 c.c. of Solution.	Temp.	Specific Rotation. $[\alpha]_D$
0·531	20°	+ 4·36
1·880	32	+ 3·78
1·875	40	+ 3·04
1·873	50	+ 1·55
1·857	60	+ 1·22
1·838	75	0
1·835	77	− 0·61
1·830	80	− 0·76
1·825	90	− 1·86

A. H.

Selenic Anhydride. By RENÉ METZNER (*Compt. rend.*, 1896, **123**, 1061—1063).—In a previous paper (this vol., ii, 132), the author has shown that the heats of combination of hydrogen selenate with one molecule of water (+ 9·1 Cal.) and of dissolution of the same acid (+ 16·8 Cal.) were approximately equal to the corresponding numbers for hydrogen sulphate. Assuming that the analogy holds good for the heats of combination of the anhydrides with one molecule of water, this number would be + 19·6 Cal. for selenic acid, from which + 42·1 Cal. is deduced as the heat of formation of selenic anhydride, a number which is smaller than the heat of formation of selenious anhydride from its elements. The endothermic nature of the formation of selenic anhydride from selenious anhydride and oxygen explains the failure of the attempts made hitherto to isolate it, as well as the ready formation of selenious anhydride and oxygen, when hydrogen selenate is heated with phosphoric anhydride under reduced pressure at 210—220°. This is also confirmed by a comparison of the two following thermic equations.

$$SeO_2 + O + H_2O = H_2SeO_4 \text{ liq.} \quad + 3{\cdot}06 \text{ Cal.}$$
$$SO_2 + O + H_2O = H_2SO_4 \text{ ,,} \quad + 56{\cdot}4 \text{ ,,}$$

A. C. C.

Automatic Cut-off of Gas on Stoppage of the Water Supply. By HUGO MICHAELIS (*Ber.*, 1897, **30**, 282—284).—The author

describes a simple apparatus by means of which the gas supply to burners which are employed for heating water baths, &c., may be automatically shut off when the water supply is by any accident stopped. A tap is inserted in the gas supply pipe, and is attached to a balanced lever, one arm of which carries a funnel through which the water supply has to pass. So long as this funnel is full, or overflowing, the lever remains horizontal and the gas tap is open, but as soon as the water supply ceases, the funnel empties itself through a small hole at the apex, the counterpoise falls, and the gas tap is closed. A. H.

Apparatus for Filtering and Drying Substances Unstable in presence of Air. By TASSILLY (*Bull. Soc. Chim.*, 1896, [3], **15**, 274—275).—The apparatus consists mainly of two filtering funnels, ground to fit tightly one on the other. Hydrogen, or some other inactive gas, is passed into the apparatus through the tube of the top funnel. M. W. T.

Inorganic Chemistry.

Structural Isomerism in Inorganic Compounds. By ALEXANDER P. SABANÉEFF (*Ber.*, 1897, **30**, 285—287).—*Hydroxylamine hypophosphite*, NH_3O,H_3PO_2 can be obtained by the action of hydroxylamine sulphate on barium hypophosphite in an atmosphere of carbonic anhydride. Decomposition occurs when the solution is heated on the water bath, but, on spontaneous evaporation, needle-shaped crystals of the salt are deposited. It is hygroscopic, and melts at about 92°, occasionally exploding when heated. In dilute solution, it appears to be largely dissociated into its ions. This salt is isomeric (metameric) with ammonium dihydrogen phosphite (Amat, Abstr., 1888, 107), which melts at 123° and forms monosymmetric crystals.

The author claims this as the first well-defined instance of structural isomerism among inorganic compounds, and proposes to further investigate the metameric salts of the nitrogen bases. A. H.

Note.—The isomeric sodium potassium sulphites (Röhrig, *J. pr. Chem.*, [2], **37**, 217) and thiosulphates (Schwicker, Abstr., 1889, 942) are also instances of structurally isomeric inorganic compounds. A. H.

Combustion of Coal Gas in Gas Engines. By FRITZ HABER and A. WEBER (*Ber.*, 1897, **30**, 145—151).—The authors have examined the spent gases obtained from two varieties of gas engine. When working at full pressure, no appreciable amount of inflammable gas escapes, the product consisting, for the most part, of carbonic anhydride; at half-pressure, however, a considerable amount of an inflammable gas is evolved, consisting largely of carbonic oxide.

J. F. T.

The Artificial Colouring of Crystals of the Haloid Salts of the Alkali Metals by means of Sodium and Potassium vapour. BY FRITZ GIESEL. (*Ber.*, 1897, **30**, 156—158).—The similarity between

the colour of blue rock salt and that produced by the action of the cathode rays on crystals of sodium chloride, seemed to suggest the possibility of colouring these crystals by purely chemical means and this is, in fact, readily effected by heating them in a closed tube with sodium or potassium vapour, the colour produced being independent of the metal used.

Under these conditions, potassium bromide and iodide are coloured deep blue; potassium chloride, dark heliotrope, and sodium chloride, yellow to brown, the colour appearing to pervade the whole crystal and not merely to reside on the surface; it is stable in the air, and even in water is retained as long as the crystal remains undissolved, the solution, however, is colourless, and a colourless salt is obtained on evaporating it. At high temperatures, the colour is discharged.

The behaviour of the yellowish-brown sodium chloride is remarkable. On heating, the colour passes gradually from yellow through red to bluish violet, ultimately becoming colourless, but any shade of colour can be retained by cooling at the moment of its production. It is possible, therefore, to obtain a blue shade identical with that of the naturally occurring blue rock salt.

The blue colour of sodium chloride crystals obtained by the action of the cathode rays, and also that of blue rock salt, can be changed into yellow or red under the same conditions, the only difference being that, in the latter, a red fluorescence is always apparent. J. F. T.

Metallic Precipitation. By JEAN B. SENDERENS (*Bull. Soc. Chim.*, 1896, [4], 15, 208—221. Compare Abstr., 1896, ii, 106).—The author shows experimentally that when one metal is precipitated from a solution of its nitrate by another metal, the amount of the second metal which goes into solution is more than can be accounted for by the reaction $R''(NO_3)_2 + M'' = M''(NO_3)_2 + R''$.

In the case of copper or cobalt in contact with solutions of silver nitrate, the excess is very slight, and becomes negligable when air is excluded from the apparatus during the experiment. In most cases, however, the metal becomes oxidised at the expense of the nitric acid present, forming a hydroxide or basic nitrate. M. W. T.

Nickelo-nickelic Hydroxide. By WILLIAM L. DUDLEY (*J. Amer. Chem. Soc.*, 1896, 18, 901—903).—Nickelo-nickelic hydroxide, $Ni_3O_4,2H_2O$, is obtained by fusing sodium peroxide with metallic nickel in a nickel crucible, at a cherry-red heat. The action is nearly complete at the end of an hour; when cold, the mass is extracted with water, and the crystals which remain are washed several times with boiling water. The last traces of alkali are only removed after some 50 hours' washing with water in a Soxhlet extraction apparatus. Metallic nickel may be removed by means of a magnet. It is uncertain whether the water is derived from sodium hydroxide in the sodium peroxide, or is taken up during the extraction with water. The crystals are lustrous, and almost black, with a slight brownish-bronze hue. They are soft, and dissolve in acids, forming nickelous salts. Water and alkalis have no action. The sp. gr. of the compound is 3·4115 at 32°. When heated to 140°, it begins to lose weight; at 240° the weight remains constant; but at a red heat

further loss is sustained, and nickelous oxide is formed. The compound made in an ordinary nickel crucible usually contains a small amount of cobalt. J. J. S.

Sulphides of Cobalt and Nickel. By GABRIEL CHESNEAU (*Compt. rend.*, 1896, **123**, 1068—1071. Compare Abstr., 1895, ii, 228, 247).—When sodium monosulphide is added to a solution of cobaltous chloride, the precipitated sulphide is completely insoluble in an excess of the precipitant. If, however, a solution of the monosulphide saturated with sulphur at the ordinary temperature (containing about 3·7 eq. of sulphur for 1 eq. of sodium) is employed, a black precipitate is obtained, which, although quite insoluble in sodium monosulphide, dissolves in the polysulphide solution to the extent of 6 grams of cobalt per litre at the ordinary temperature. In sodium polysulphide solutions which are not saturated with sulphur, the solubility of the cobalt sulphide very rapidly diminishes. Cobaltous sulphide itself only dissolves in the polysulphide solution to the extent of 0·35 gram of cobalt per litre, the greater solubility of the above-mentioned precipitate being due to the fact that it consists of a persulphide of cobalt probably having the formula Co_2S_7. On evaporating the solution of cobalt persulphide in sodium polysulphide in a vacuum, black, crystalline plates separate, which are deliquescent and soluble in water and absolute alcohol, but which were not analysed.

When sodium polysulphide is added to a solution of a nickel salt, a black persulphide is obtained, apparently corresponding with the cobalt compound; this, however, differs from it in being appreciably soluble in the monosulphide and practically insoluble in the polysulphide solution. A. C. C.

Sulphochromic Acid, a New Acid containing Chromium. By ALBERT RECOURA (*Bull. Soc. Chim.*, 1896, [3], **15**, 315—321).—Compounds of chromium sulphate with 1, 2, or 3 molecules of sulphuric acid have already been described (Abstr., 1893, ii, 470). By evaporating a solution containing 1 molecule of chromium sulphate to 3, 4, or 5 molecules of sulphuric acid, and heating the product for a day or two at 115°, the following substances separated in crystals—$Cr_2(SO_4)_3$, $4H_2SO_4$, $Cr_2(SO_4)_3$, $5H_2SO_4$, $Cr_2(SO_4)_3$, $6H_2SO_4$. (Compare Abstr., 1893, ii, 528.) On heating the solutions of these substances in water, or leaving them for some days, they deposit a flocculent precipitate of a greenish colour; the addition also of a salt of any metal, even of sodium or potassium, to the original solution, produces a precipitate.

As, from their properties, the three compounds appeared to contain the same central group, the compound $Cr_2(SO_4)_3,4H_2SO_4$ was taken for investigation. On adding a molecular equivalent of cupric chloride to a solution containing a known quantity of this compound, a whitish-green precipitate was formed having the composition $Cr_2O_3,CuO,4SO_3$, but evidently differing from copper chromium sulphate, which is a soluble salt. The compound, when boiled with 8 equivalents of sodium hydroxide, gave sodium sulphate and copper chromite, Cr_2O_3, CuO. This may be taken as indicating that, in the compound $Cr_2O_3,CuO,4SO_3$, the copper is directly united to the chromium, and not to the SO_3 group. As to the

manner in which the remaining molecules of sulphuric acid, which are left in solution on adding a metallic salt to a solution of $Cr_2(SO_2)_3,4H_2SO_4$ are combined, nothing has been ascertained.

Potassium salts behave in the same manner as copper salts, forming a compound $Cr_2O_3,K_2O,4SO_3$. To these compounds the author has given the name sulphochromites.

Sulphochromic acid (compare Abstr., 1896, ii, 27).—When heated to 140—150°, the compound $Cr_2(SO_4)_3,4H_2SO_4$ loses 3 molecules of sulphuric acid, and sulphochromic acid, $(SO_3)_4Cr_2O_2(OH)_2$, is formed; this is a grey, amorphous substance, soluble in water, and giving a precipitate $(SO_3)_4,Cr_2O_3,OM''$ with metallic salts. Its heat of neutralisation is higher than that of sulphuric acid,

$(SO_4)_4Cr_2O_2(OH)_2$ diss. + Na_2SO_4 diss. = $(SO_4)_4Cr_2O_2(ONa)_2$ diss.
+ H_2SO_4 diss. .... + 5·1 Cal.,

the presence of the SO_3 groups in the compound having a powerful influence on the nature of the hydroxyl groups.

The paper concludes with a note on the isomerism of the sulphochromites and the compounds derived from hydrogen chromium sulphate, and a short note on the preparation of chromites. M. W. T.

The Silicotungstates. By GREGOIRE N. WYRUBOFF (*Bull. Soc. franc. min.*, 1896, **19**, 219—354).—The fact that valuable information of a purely chemical nature, as opposed to information of a physico-chemical character, respecting the valency of the metals can be obtained by a study of the crystallographical properties of their salts, has led the author to make an exhaustive examination of the silicotungstates. In order to determine the valency of a metal, crystallographical evidence of a positive kind must be obtained; it is not legitimate to conclude that a metallic oxide is not a sesquioxide because its sulphate does not form an alum with the alkali sulphates, neither is cadmium to be regarded as not a member of the magnesium group because its sulphate yields none of the hydrates characteristic of the group; and since the author has found that the metals display their distinctive properties most fully in their more complex compounds, he has studied the salts of silicotungstic acid, which have high molecular weights, crystallise well, and are very stable, in order to extend our knowledge of valency.

Silicotungstic acid is best prepared from commercial sodium tungstate by a modification of Marignac's process (*Ann. chim. phys.*, 1864, [4], **3**, 5); nitric acid is added to the concentrated aqueous solution of the salt until the precipitate first formed is just dissolved, and after adding excess of gelatinous silica, the liquid is heated, being kept acid by occasionally adding nitric acid, until a test sample is no longer precipitated by hydrochloric or nitric acid; if the heating be too prolonged, silicodecitungstic acid is formed. After filtration, mercurous nitrate, free from mercuric salt, is added, and the precipitate is washed by decantation and decomposed by hot hydrochloric acid; the filtered solution yields pure silicotungstic acid on evaporating to dryness.

Marignac considered silicotungstic acid to be octobasic, having the composition $12WO_3,SiO_2,4H_2O$, because of its behaviour towards carbonates; the author finds, however, that its salts containing $2R_2O$ only

decompose the carbonates of the alkalis, alkaline earths, and magnesium, and also that, until the acid attains the composition $12WO_3,SiO_2,2H_2O$ or $H_4W_{12}SiO_{40}$ (at 370°) it preserves all its properties; the acid must therefore have the latter composition and be tetrabasic. It decomposes nitrates and chlorides, and is only partially decomposed by prolonged boiling with sulphuric acid, it is, however, very readily oxidised by protosalts; it forms salts with all the uni-, bi-, and tri-valent metals, but not with the tetrad metals. The normal and acid salts usually crystallise well and are extremely soluble in water, alcohol or ether, forming with the last two solvents stable compounds which have not yet been examined.

Silicotungstic acid crystallises below 40° in large, efflorescent tetragonal octahedra [$a : c = 1 : 1·0117$] of the composition $H_4W_{12}SiO_{40} + 31H_2O$; this hydrate is analogous in composition to the cubic silicotungstates of the trivalent metals, and morphotropically closely related to them in that it is very nearly cubic and almost isotropic. Above 40°, or from a hydrochloric or nitric acid solution, rhombohedral crystals [$a : c = 1 : 2·4719$] of a hydrate containing $24H_2O$ are obtained; they are isomorphous with the silicotungstates of the alkaline earths containing $24H_2O$.

The silicotungstates of the univalent metals are not isomorphous amongst themselves, but differ in degree of hydration and other properties; the solubility both of the normal, acid, and basic salts diminishes rapidly as the atomic weight of the metal increases. The hydrates of the three classes of salts contain less water than the salts of the bi- or tri-valent metals; the silicotungstates of the univalent metals never crystallise with more than $20H_2O$, those of the alkaline earths never crystallise with more than $24H_2O$, those of the magnesium group never combine with more than $27H_2O$, whilst the silicotungstates of the trivalent metals do not crystallise with more than $31H_2O$. It is consequently concluded that, if an oxide RO having a molecular weight greater than 100 forms sparingly soluble silicotungstates containing not more than $20H_2O$, the metal is univalent.

Ammonium forms two colourless, amorphous silicotungstates of the composition $(NH_4)_4W_{12}SiO_{40} + 8H_2O$ and $(NH_4)_4W_{12}SiO_{40},4NH_4·OH + 14H_2O$, but yields no acid salt. The minutely crystalline basic sodium salt, dried at 100°, has the composition $Na_4W_{12}SiO_{40},4NaHO + 5H_2O$. The normal salt, $Na_4W_{12}SiO_{40} + 20H_2O$, is dimorphous, crystallising in a stable anorthic form [$a : b : c = 1·0320 : 1 : 0·9092$. $\alpha = 94°2'$. $\beta = 93°32'$. $\gamma = 88°21$] and in an unstable anorthic form [$a : b : c = 0·8056 : 1 : 1·1221$. $\alpha = 93°14'$. $\beta = 103°29'$. $\gamma = 88°3'$]; it readily changes into a third anorthic *hydrate* containing $14H_2O$ [$a : b : c = 1·6083 : 1 : 0·5542$. $\alpha = 90°52'$. $\beta = 95°22'$. $\gamma = 83°34'$], which also crystallises at 35°. Above 40°, or in presence of hydrochloric or nitric acid, an anorthic hydrate of the composition $Na_4W_{12}SiO_{40} + 13H_2O$ crystallises [$a : b : c = 1·0932 : 1 : 0·9102$. $\alpha = 88°51'$. $\beta = 95°18'$. $\gamma = 86°37'$.] On crystallising the salt from a feebly acid solution at 25—30°, beautiful anorthic plates of the composition $Na_2H_2W_{12}SiO_{40} + 16H_2O$ are deposited [$a : b : c = 1·0748 : 1 : 0·9521$. $a = 1·0748 : 1 : 0·9521$. $\alpha = 89°6'$. $\beta = 95°50'$. $\gamma = 85°17'$]. The double salt of the composition $3Na_4W_{12}SiO_{40},4NaNO_3 + 45H_2O$ is also anorthic [$a : b : c = 1·0057 : 1 : 0·8562$. $\alpha = 89°35$. $\beta = 90°20'$. $\gamma = 91°6'$].

The double potassium salt, $K_4W_{12}SiO_{40},4KHO + 12H_2O$, is soluble in 10 parts of water at 18° and is only indistinctly crystalline. The hexagonal [$a : c = 1 : 0·5500$] hydrate, $K_4W_{12}SiO_{40} + 18H_2O$, loses $12H_2O$ in the air and becomes anhydrous at 105°; the crystals are circularly polarising and are always dextrorotatory, $\alpha_D = 14°4'$. A nitric acid solution at temperatures above 30°, deposits a monosymmetric [$a : b : c = 1·4715 : 1 : 1·9939$. $\beta = 77°6'$] *hydrate*, $K_4W_{12}SiO_{40} + 15H_2O$ and a sulphuric acid solution at 30—34° deposits a monosymmetric [$a : b : c = 1·2148 : 1 : 0·8489$. $\beta = 77°44'$] double salt of the composition $K_4W_{12}SiO_{40},K_2H_2W_{12}SiO_{40} + 29H_2O$.

The *acid rubidium* salt, $Rb_4W_{12}SiO_{40},Rb_2H_2W_{12}SiO_{40} + 22H_2O$ is obtained as an amorphous, white powder, and on treating it with nitric acid and washing with water an amorphous *salt*, $Rb_2H_2W_{12}SiO_{40} + 5H_2O$ is obtained. The *thallium* salt, $Tl_2H_2W_{12}SiO_{40} + 9H_2O$, is also amorphous; the silver salt, $Ag_4W_{12}SiO_{40} + 9H_2O$, is very sparingly soluble and loses $4H_2O$ at 105°. The mercurous salt,

$$Hg_4W_{12}SiO_{40},2Hg_2O + 5H_2O$$

is quite insoluble.

The author considers lithium to be a bivalent metal of atomic weight 14 for the following reasons. Its chloride, nitrate and thiosulphate only are isomorphous with the corresponding sodium salts, and it does not displace the alkali metals from their combinations but readily forms double salts with them; the simple reactions of lithium are also very similar to those of the alkaline earths and very different from those of the alkali metals. Further indication of the bivalency of lithium is found in its affinity for nitrogen, the impossibility of reducing its hydroxide by metals like iron, the sparing solubility of its hydroxide in alcohol and water, the non-existence of a bicarbonate, the instability of its acid sulphate, the ready decomposition of its nitrate by heat, the solubility in alcohol and sparing solubility in nitric acid of its nitrate, the insolubility and decomposition by heat of its carbonate and the insolubility of its fluoride, phosphate, and silicate; the bivalency of lithium is contrary to Dulong and Petit's law and to the periodic law, but to these the author attaches little weight. It is now shown that *lithium silicotungstate*, $Li_2W_{12}SiO_{40}$, is an extremely soluble salt isomorphous with the silicotungstates of barium and calcium; it crystallises in the rhombohedral system [$a : c = 1 : 2·6186$] as a *hydrate* containing $24H_2O$ which is isomorphous with and crystallises in all proportions with the acid. On crystallisation at 40—45° from a nitric acid solution, an anorthic *hydrate* [$a : b : c = 1·1642 : 1 : 0·9681$. $\alpha = 90°$. $\beta = 94°20'$. $\gamma = 86°26'$] containing $14H_2O$ is deposited; it is isomorphous with the hydrate of the sodium salt containing $13H_2O$.

The very soluble acid calcium salt was unsuitable for examination, but the normal salt, $Ca_2W_{12}SiO_{40}$, crystallises at ordinary temperatures in large pseudohexagonal, monosymmetric crystals [$a : c = 1 : 2·6419$] containing $27H_2O$; in presence of nitric or sulphuric acid, a *hydrate* containing $24H_2O$ separates in hexagonal crystals [$a : c = 1 : 2·5045$] whilst at 30°, in presence of nitric acid, an anorthic *hydrate* [$a : b = 0·4228 : 1$. $\alpha = 87° 40'$. $\beta = 90°30'$. $\gamma = 81°6'$] containing $18H_2O$ is deposited. The double *salt*, $Ca_2W_{12}SiO_{40},Ca(NO_3)_2$, crystallises with

$15H_2O$ in monosymmetric prisms [$a:b:c = 0·9036:1:1·1820$. $\beta = 85°8'$] and with $13H_2O$ in anorthic crystals; it is decomposed by water.

The *strontium* salt, $Sr_2W_{12}SiO_{40}$, crystallises below 30° with $27H_2O$ in rhombohedra [$a:c = 1:2·5933$] and at 30°, in presence of nitric acid, in anorthic crystals [$a:b:c = 1·0212:1:0·5947$. $\alpha = 92°46'$. $\beta = 91°16'$. $\gamma = 95°18'$] containing $23H_2O$, and also in monosymmetric crystals [$a:b:c = 1·3001:1:1·0058$. $\beta = 83°14'$] containing $17H_2O$; above 50° a monosymmetric *hydrate* [$a:b:c = 1·8452:1:1·5695$. $\beta = 75°24'$] containing $16H_2O$ is obtained.

The basic barium salt contains 4 BaO; the normal salt $Ba_2W_{12}SiO_{40}$, crystallises at 30° in hexagonal prisms [$a:c = 1:2·6813$] containing $24HO_2$ and above 30° in monosymmetric crystals [$a:b:c = 1·7987:1:1·5440$. $\beta = 76°7'$] containing $16H_2O$. The *potassium barium* salt, $K_2Ba_2W_{12}SiO_{40} + 17H_2O$, crystallises in monosymmetric plates [$a:b:c = 0·6471:1:0·6056$. $\beta = 81°15'$].

The normal silicotungstates of cerium, lanthanum, and didymium crystallise with $27H_2O$, and are completely isomorphous with the corresponding hydrate of the calcium salt; all are monosymmetric and pseudorhombohedral. It follows that these three rare metals are bivalent and constitute a family very similar to that of the alkaline earths. Thorium silicotungstate also crystallises with $27H_2O$ as a pseudorhombohedral monosymmetric hydrate, and is, therefore, also bivalent; in the following formulæ, the atomic weights Ce = 93, La = 92, Di (Nd and Pr) = 96, and Th = 116 are consequently chosen. Many other arguments, both chemical and crystallographical, are quoted in favour of the bivalency of these metals.

Cerosoceric hydroxide, $Ce_3O_4,3H_2O$, is not soluble in silicotungstic acid, but dissolves on adding nitric acid giving a cerous silicotungstate; *basic cerous silicotungstate*, obtained by the action of a cerous salt on the basic sodium salt, is an insoluble, gelatinous, yellow precipitate. *Cerous silicotungstate*, $Ce_2W_{12}SiO_{40}$, crystallises below 15° with $27H_2O$ in colourless, monosymmetric plates [$a:b:c = 1·7090:1:2·6558$. $\beta = 89·40'$], whilst at 35° the same hydrate is obtained in rhombohedra [$a:c = 1:2·6820$] which become monosymmetric on cooling. The acid *salt*, $Ce_2W_{12}SiO_{40},CeH_2W_{12}SiO_{40} + 34H_2O$, crystallises below 35° from a nitric acid solution in yellow, anorthic crystals [$a:b:c = 0·3922:1:0·4195$. $\alpha = 90°43'$. $\beta = 92°20'$. $\gamma = 84°38'$].

The normal *lanthanum* salt, $La_2W_{12}SiO_{40}$, crystallises with $27H_2O$ in colourless, efflorescent rhombohedra [$a:c = 1:2·6392$]; the monosymmetric form could not be isolated. The acid *salt*,

$$La_2W_{12}SiO_{40},LaH_2W_{12}SiO_{40} + 34H_2O,$$

forms greenish, anorthic crystals [$a:b:c = 0·4081:1:0·4420$. $\alpha = 89°43'$. $\beta = 93°8'$ $\gamma = 84°29'$].

The normal *didymium* salt, $Di_2W_{12}SiO_{40}$, like the cerium salt, crystallises with $27H_2O$ below 20° in amethyst-red, monosymmetric plates [$a:b:c = 1·7000:1:2·6325$. $\beta = 89°46'$] and also in an unstable rhombohedral form [$a:c = 1:2·6660$]; above 20°, a *hydrate* containing $26H_2O$ is obtained in rhombohedral plates [$a:c = 1:1·6636$]. The acid *salt*, $Di_2W_{12}SiO_{40},DiH_2W_{12}SiO_{40} + 34H_2O$, is of darker colour [$a:b:c = 0·4003:1:0·4262$. $\alpha = 89°58'$. $\beta = 92°48'$. $\gamma = 83°20'$].

The basic *thorium* salt is insoluble, but the normal *salt*, $Th_2W_{12}SiO_{40}$, is very soluble and crystallises with $27H_2O$ like the preceding salts; the rhombohedral form only was measured [$a:c = 1:2{\cdot}6653$]. The acid *salt*, $Th_2W_{12}SiO_{40},2H_4W_{12}SiO_{40}$, crystallises with $45H_2O$ in small, anorthic prisms [$a:b:c = 1{\cdot}0721:1:1{\cdot}1403$. $\alpha = 95°47'$. $\beta = 90°6'$. $\gamma = 90°16'$].

A mixture of yttria earths from monazite having the molecular weight $RO = 88{\cdot}6$, and consisting mainly of yttria and erbia with a little terbia, was used for preparing the following two salts. The normal *salt*, $(Y,Er)_2W_{12}SiO_{40} + 26H_2O$, crystallises in rose-coloured rhombohedra [$a:c: = 1:1{\cdot}7282$] and on crystallising its solution at 30° with nitric acid, anorthic twin crystals [$a:b:c = 0{\cdot}9760:1:0{\cdot}9967$. $\alpha = 92°23'$. $\beta = 91°50'$. $\gamma = 88°22'$] of the acid *salt*,

$$(Y,Er)_2W_{12}SiO_{40},(Y,Er)H_2W_{12}SiO_{40} + 50H_2O,$$

are obtained.

The metals of the magnesium group are characterised by forming normal salts crystallising with $27H_2O$ in the rhombohedral system and by not forming sesqui-acid salts; most of them also yield anorthic hydrates containing $18H_2O$; the axial ratios for both these hydrates are given in the appended table. The rhombohedral salts are very efflorescent, and are obtained at a lower temperature than the anorthic ones.

R	$R_2W_{12}SiO_{40} + 27H_2O$	$R_2W_{12}SiO_{40} + 18H_2O$.			
	$a:c$	$a:b:c$	α	β	γ
Mg	1 : 2·6600	0·4068 : 1 : 0·4021	86° 50′	90° 35′	90° 11′
Mn	1 : 2·6549	0·4018 : 1 : 0·4088	87 0	90 11	91 0
Co	1 : 2·6760	0·4067 : 1 : 0·4055	87 9	91 8	89 23
Ni	1 : 2·6392	0·4054 : 1 : 0·4166	86 48	91 6	89 32
Cu	1 : 2·6706	—	—	—	—
Zn	1 : 2·6279	0·4034 : 1 : 0·3911	86 6	91 26	91 5
Cd	1 : 2·6123	—	—	—	—

A very efflorescent cupric salt containing $29H_2O$ is obtained below 10°; from 10—40°, the $27H_2O$ hydrate is obtained, and above 40° the hydrate with $18H_2O$. In like manner, the zinc salt crystallises with 29 H_2O at 10°, with $27H_2O$ at 10—25°, and with $18H_2O$ above 25°. The *cadmium* salt is obtained as an anorthic hydrate [$a:b:c = 0{\cdot}3784:1:0{\cdot}3207$. $\alpha = 88°7'$ $\beta = 96°9'$. $\gamma = 89°31'$] containing $23H_2O$ by evaporating its nitric acid solution at 30°; a *salt* of the composition

$$2Cd_2W_{12}SiO_{40},H_4W_{12}SiO_{40} + 42H_2O$$

was also prepared.

The *mercuric* salt, $Hg_2W_{12}SiO_{40}$, is extremely soluble and crystallises at 25° in anorthic prisms [$a:b:c = 0{\cdot}9848:1:1{\cdot}0191$. $\alpha = 97°40'$. $\beta = 94°22'$. $\gamma = 90°40'$] containing $15H_2O$; its solution decomposes on boiling, giving an insoluble basic salt and silicotungstic acid. The *lead* salt, $Pb_2W_{12}SiO_{40} + 21H_2O$, is obtained under certain conditions

and forms monosymmetric crystals. [$a:b:c = 1{\cdot}7963:1:1{\cdot}1203$. $\beta = 81°35'$]. The basic *salt*, $Pb_2W_{12}SiO_{40},2PbO + 20H_2O$, is a sparingly soluble, amorphous powder.

The normal silicotungstates of the trivalent metals give a cubic hydrate with $31H_2O$ at ordinary temperatures, and at 30—35° a hydrate containing $29H_2O$ isomorphous with the $27H_2O$ hydrates of the magnesium series; at higher temperatures, a monosymmetric hydrate with $20H_2O$ is usually obtained. The trivalent metals do not form sesqui-acid tungstates, but they give extremely soluble, uncrystallisable basic salts. On adding ammonia to the solution, a precipitate is obtained soluble in excess of the reagent. The author shows that beryllium possesses the properties characteristic of the trivalent metals, and therefore concludes that, in spite of the chemical evidence, beryllia has the composition Be_2O_3.

Beryllium silicotungstate, $Be_4(W_{12}SiO_{40})_3$, crystallises below 45° as a cubic hydrate containing $93H_2O$, and above 45° as a rhombohedral hydrate [$a:c = 1:2{\cdot}4282$] containing $87H_2O$; in presence of nitric acid at 30°, a hydrate containing $45H_2O$ is obtained. Aluminium yields a cubic *hydrate* with $93H_2O$, and a rhombohedral *hydrate* [$a:c = 1:2{\cdot}6655$] with $87H_2O$, whilst the nitric acid solution deposits a monosymmetric *hydrate* [$a:b:c = 0{\cdot}8521:1:1{\cdot}0894$. $\beta = 73°20'$] containing $60H_2O$ at 35°. *Chromium silicotungstate*, $Cr_4(W_{12}SiO_{40})_3$, gives the $93H_2O$ hydrate below 25° and the rhombohedral hydrate [$a:c = 1:2{\cdot}5354$] with $87H_2O$ above 25°, whilst the monosymmetric hydrate [$a:b:c = 0{\cdot}8658:1:1{\cdot}0798$. $\beta = 73°44'$] with $6H_2O$ is deposited by the nitric acid solution at 30°. *Ferric silicotungstate* yields the cubic hydrate with $93H_2O$ and the monosymmetric hydrate [$a:b:c = 0{\cdot}8465:1:1{\cdot}0897$. $\beta = 73°20'$] with $60H_2O$, but the hydrate with $87H_2O$ could only be obtained as an isomorphous mixture with the corresponding aluminium salt. *Gallium silicotungstate*, $Ga_4(W_{12}SiO_{40})_3$, gives the cubic hydrate with $93H_2O$, the rhombohedral salt [$a:c: = 1:2{\cdot}6346$] with $87H_2O$, and the monosymmetric hydrate [$a:b:c = 0{\cdot}9057:1:1{\cdot}1585$. $\beta = 74°20'$] with $60H_2O$.

The behaviour of the uranium silicotungstates makes it probable that uranic oxide has the composition U_2O_3 and that the metal has an atomic weight of 120. On heating silicotungstic acid solution with different quantities of uranic nitrate, evaporating off the nitric acid, and crystallising, a series of crystalline cubic salts of the following compositions (U = 120) was obtained.

$$U_4(W_{12}SiO_{40})_3 + 87H_2O,2U_2H_6(W_{12}SiO_{40})_3 + 174H_2O.$$
$$U_4(W_{12}SiO_{40})_3 + 87H_2O,U_2H_6(W_{12}SiO_{40})_3 + 87H_2O.$$
$$2U_4(W_{12}SiO_{40})_3 + 174H_2O,U_2H_6(W_{12}SiO_{40})_3 + 87H_2O.$$
$$U_4(W_{12}SiO_{40})_3 + 87H_2O.$$
$$U_4(W_{12}SiO_{40})_3 + 87H_2O,U_2O_3,H_2O + 87H_2O.$$
$$U_4(W_{12}SiO_{40})_3 + 87H_2O,3U_2O_3,3H_2O + 261H_2O.$$
$$U_4(W_{12}SiO_{40})_3 + 87H_2O,4U_2O_3,4H_2O + 348H_2O.$$

W. J. P.

Antimonic Tungstates. By L. A. HALLOPEAU (*Compt. rend.*, 1896, **123**, 1065—1068).—When an excess of antimonic acid is boiled for several hours with a solution of potassium paratungstate, it dissolves,

and, on filtering, crystals of potassium antimoniotungstate are deposited having the composition $2WO_3,3KSbO_3 + 8H_2O$, and differing from the antimoniotungstate described by Gibbs. This compound forms small botryoidal masses, composed of a very large number of prismatic, twinned crystals, which are highly refractive and act powerfully on polarised light. They are permanent in the air, lose $6H_2O$ at 100°, and, on ignition, yield potassium tungstate, tungstic acid, and antimonic acid. When fused with an excess of sodium carbonate, carbonic anhydride is evolved and sodium tungstate, potassium tungstate and trisodium antimonate are formed. On treating the fused mass with water, a crystalline sodium antimonate, $Sb_2O_5,Na_2O + 6H_2O$, is left. Potassium antimoniotungstate is decomposed by hydrochloric, sulphuric, and nitric acids with formation of tungstic acid, and by hydrogen sulphide with precipitation of antimony and tungsten. When well-washed silver antimoniotungstate is treated with the theoretical quantity of hydrochloric acid, and the solution evaporated in a vacuum, a transparent, vitreous, residue of *antimoniotungstic acid*, $4WO_3,3Sb_2O_5,3H_2O + 8H_2O$, remains, which does not lose weight at 100°.

A. C. C.

Mineralogical Chemistry.

Heavy Liquids for the Separation of Minerals. By JAN W. RETGERS (*Jahrb. f. Min.*, 1896, ii, 183—195. Compare this vol., ii, 45). —The author gives the results of experiments made with the object of finding amongst the nitrates and double nitrates of the heavy metals (silver, mercury, lead and thallium) a heavy liquid suitable for the separation of minerals, especially sulphides. In many cases, these are unsuitable, owing, usually, to their easy decomposition. Those found to be the more suitable are the following.

Mercurous nitrate, $HgNO_3 + H_2O$, melts at 70° to a clear, mobile liquid of sp. gr. 4·3; it is miscible with water, and is much less expensive than the other salts; basic nitrates, however, separate on heating.

Thallium nitrate (m. p. 205°, sp. gr. 5·3) does not mix with water, and, like the thallium silver nitrate (m. p. 70°, sp. gr. 4·8), it acts on sulphides. Thallium mercuric nitrate (m. p. 110°, sp. gr. 5·0) does not act on sulphides, but the liquid is cloudy.

Thallium mercurous nitrate (m. p. 76°, sp. gr. 5·3) gives a clear, mobile liquid, which is miscible with water and does not act on sulphides; this is the most convenient liquid described, and ought to be very useful in the separation of mineral sulphides, which so often enclose impurities. L. J. S.

Occurrence of Rubies in Burma. By MAX BAUER (*Jahrb. f. Min.*, 1896, ii, 197—238).—Material from the Sagyin (Sadschijin)

Hills, which are about 20 miles north of Mandalay, is described. Here ruby occurs in a white, crystalline marble with spinel, chondrodite apatite, phlogopite, hornblende, pyrites, pyrrhotite and graphite. The marble is usually dolomitic, although at times magnesium is absent; the mean of two analyses is

CO_2.	CaO.	MgO.	Insol.	Total.	$CaCO_3$.
44·5	48·65	6·4	0·2	99·75	$86\frac{2}{3}$

The well-developed crystals of ruby have rounded edges and show etch figures, but are not surrounded by alteration products: a detailed crystallographic description is given; lamellar twinning on *c*(111) and *r*(100) is rare; *e*{110} is given as a new form. The chondrodite occurs plentifully as irregular grains; analysis of fresh material of a greenish yellow colour gave

SiO_2.	MgO.	FeO.	Al_2O_3.	CaO.	F.	H_2O.	Total.	Sp. gr.
37·41	47·90	7·40	2·60	0·90	1·15	1·23	98·59	3·197

The sp. gr. of dull, weathered material is 3·175, and of white material still more weathered 3·138.

According to the observations of Noetling, the limestone is of organic origin, and is of wide distribution in Burma; it has become crystalline, and the various minerals have been developed in it, by the action of contact metamorphism. This mode of origin of the limestone and rubies is quite different from that put forward by Brown and Judd (Abstr., 1896, ii, 32) in their description of the adjoining Mogok district.

In a general review of the modes of occurrence of ruby and sapphire, it is pointed out that these two varieties of corundum do not, as a rule, occur together: ruby usually occurs in crystalline limestone with spinel, whilst sapphire is more characteristic of granites and crystalline schists and is not associated with spinel. The sapphires found in volcanic rocks are probably foreign enclosures derived from granites, &c.

L. J. S.

Chemical Nature of Vesuvian [Idocrase]. By CARL F. RAMMELSBERG (*Jahrb. f. Min.*, 1896, ii, 157—164).—Reducing the bases to the equivalent R′, the mean ratios deduced from 41 published analyses are $R' : Si = 4·44 : 1$ and $R''' : R'' = 2 : 1$, individual analyses showing, as a rule, only small variations from these means; the ratio $R' : R''$, however, varies from 1 : 1·9 to 1 : 11·0. Assuming $R' : Si = 4·5 : 1$, the formula for idocrase becomes $R'_{18}Si_4O_{17} = 3R'_4SiO_4, R'_6SiO_5$, or in detail $R'_{18}Si_4O_{17}$, $n(4R''_9Si_4O_{17}, 3R'''_6Si_4O_{17})$, where *n* is 1, 1·5, 2, or 4. In the calculations, the titanium is taken with the silica; $R' = H, K, Na$; $R'' = Ca, Mg, Fe, Mn$; $R''' = Al, B, Fe, Mn$; and fluorine has been neglected, being considered to form a fluosilicate of the same composition as the oxysilicate. Various anomalous analyses are discussed in detail, and are brought into agreement with the above formula. If the titanium be calculated as Ti_2O_3, some FeO must be omitted, as $Ti_2O_3 + Fe_2O_3 = 2TiO_2 + 2FeO$: the amount of FeO found in the analysis gives a basis for calculating the relative amounts of TiO_2 and Ti_2O_3.

L. J. S.

Theory of Plagioclase mixing. By CARL F. RAMMELSBERG (*Jahrb. f. Min.*, 1896, ii, 165—181).—If Tschermak's theory, that the plagio-

clastic felspars are isomorphous mixtures of albite ($NaAlSi_3O_8$) and anorthite ($CaAl_2Si_2O_8$), be true, then for every ratio of Na : Ca there must be a certain fixed ratio of Al : Si. This was pointed out by the author in 1872, and in the present paper he gives the ratios, calculated from numerous published analyses, of labradorite, andesine, and oligoclase, and finds that for 80 per cent. there is an agreement with theory. The cases of disagreement are to be explained by imperfect analyses and impure material; these usually show an excess of sodium over that calculated from the ratio Al : Si. These exceptions also do not agree with the theory of Sartorius von Waltershausen, that the plagioclases are mixtures of $m Na_2Al_2Si_6O_{16} + n CaAl_2Si_6O_{16}$ with $m CaAl_2Si_2O_8 + n Na_2Al_2Si_2O_8$. The simplest and most frequent mixtures are: labradorite, Ab_1An_3, Ab_1An_2; andesine, Ab_3An_4, Ab_1An_1, Ab_5An_4; oligoclase, Ab_3An_2, Ab_2An_1, Ab_3An_1. L. J. S.

Relation between Dynamometamorphism and Molecular Volume. By Friedrich Becke (*Jahrb. f. Min.*, 1896, ii, 182—183).—Comparing certain massive rocks with their dynamometamorphic representatives, it is seen that the two contain different minerals composed of the same elements; for example, porphyries with orthoclase are altered to sericite-schists. Another change can be expressed as follows

$$\underset{\text{Plagioclase.}}{x(NaAlSi_3O_8) + 4(CaAl_2Si_2O_8)} + \underset{\text{Orthoclase.}}{KAlSi_3O_8} + 2H_2O$$

$$= \underset{\text{Albite.}}{x(NaAlSi_3O_8)} + \underset{\text{Zoisite.}}{2(HCa_2Al_3Si_3O_{13})} + \underset{\text{Muscovite.}}{H_2KAl_3Si_3O_{12}} + \underset{\text{Quartz.}}{2SiO_2}.$$

Neglecting the albite molecules, the sum of the molecular volumes on the left hand side of this equation is 547·1, and on the right hand side 462·5. In the altered rock, therefore, the elements form minerals occupying the least possible space. This explains the frequent occurrence of garnet, mica, epidote, and other minerals of high specific gravity in the crystalline schists. The case of hornblende taking the place of augite and olivine seems to be an exception, but later analyses show the presence of water in this hornblende, which may then have a lower molecular volume than the corresponding augite + water.

L. J. S.

Analysis of Water from a new Iodine Spring. By Andreas Lipp (*Ber.*, 1897, **30**, 309—312).—The water of the Marien spring, situated in the parish of Seeg in Bavaria, is colourless, and has a temperature of from 7—8° at all seasons, and a sp. gr. of 1·00216 at 17°. It has a feebly alkaline reaction, and becomes slightly brown in contact with the air, owing to the separation of small quantities of free iodine. Its composition is as follows, in grams per litre—I, 0·01487; Br, 0·01178; Cl, 1·45660; SiO_2, 0·0065; Na, 0·914; CaO, 0·1605; MgO, 0·0615; Fe_2O_3, 0·00250; CO_2, combined 0·15694, free or half combined, 0·185. J. F. T.

Physiological Chemistry.

Influence of Atmospheric Oxygen on Metabolism. By Paul von Terray (*Pflüger's Archiv*, 1896, **65**, 393—446).—The total metabolic changes in dogs and rabbits are independent, within wide limits, of the composition of the inspired air; even when the oxygen was only present to the extent of 10·5 per cent., although the respirations become deeper, the nitrogen and carbonic anhydride secretion showed practically no change. The only difference at the higher limit (87 per cent. of oxygen) was an increase in the excretion of carbonic anhydride.

Below 10·5 per cent. of oxygen, the compensatory power of the body is lost, and the lack of oxygen is felt; the amount of carbonic anhydride is greatly, and of nitrogen slightly, increased. The rise in the output of carbonic anhydride cannot be explained by increase of muscular work, but is due to the entrance into the blood of organic acids; the urine contains lactic and oxalic acids, and sometimes albumin.

W. D. H.

Influence on Metabolism of dividing the Nutriment into several Meals. By Franz von Gebhardt (*Pflüger's Archiv*, 1896, **65**, 611—626).—In as pure proteid nutrition as possible, the animal becomes thinner; this is due to loss of fat, and of water. Nitrogen-apposition can be considerable, even when the loss of body weight occurs.

By dividing the nutriment into several meals daily, the organism retains more nitrogen than if all the food for the day is given in one dose. This occurs even when the digestive and absorptive powers of the alimentary tract are not unduly taxed by the single large meal. It is, therefore, advisable to divide the nutriment into several meals.

W. D. H.

Changes of the Fat of Chyle in the Blood. By Wilhelm Cohnstein and Hugo Michaelis (*Pflüger's Archiv*, 1896, **65**, 473—491).—The blood has the property of causing the disappearance of the fat of the chyle, introduced either in the natural way or by artificial injection. This depends on the presence of oxygen, and is associated with the corpuscles of the blood. The red corpuscles contain a substance which has this *lipolytic* function; the fat is changed into a substance insoluble in ether; this substance is not gaseous, but solid; water and carbonic anhydride were not found in experiments *in vitro*. The change the fat undergoes is probably saponification; but further work is in hand on the question.

W. D. H.

Course of Excretion of Nitrogen in Man. By Rudolf Rosemann (*Pflüger's Archiv*, 1896, **65**, 343—392).—The nitrogen in the urine was estimated by Kjeldahl's method in successive portions during the course of the day, the maximum occurring between 9 and 11 a.m., the minimum from 1 to 3 p.m. The influence of meals, hunger,

exercise, and other factors was also investigated, and the results are given in numerous tables. W. D. H.

Occurrence and Detection of Nucleohiston in Urine. By Adolf Jolles (*Ber.*, 1897, **30**, 172—174).—A sample of urine in a case of *pseudoleucæmia* was found to yield a voluminous precipitate with acetic acid, the relatively strong phosphorous reaction of this on the one hand, and the absence of a precipitate on saturation with magnesium sulphate on the other, seemed to indicate the presence of nucleohiston; this was isolated, and purified by dissolving it in sodium hydroxide and reprecipitating with acetic acid, the process being repeated twice. From 600 c.c. of urine, 0·1936 gram of the compound was obtained in this way, 3·14 per cent. of phosphorus being found in it by the ammonium molybdate method. A second experiment, using a larger quantity of urine, yielded a substance containing 3·25 per cent. of phosphorus; these results agree with the 3·025 per cent. observed by Lilienfeld in nucleohiston.

On treating the precipitate with dilute hydrochloric acid for some hours, and filtering, a solution was obtained which, on the one hand, gave a flocculent precipitate with ammonia, a reaction characteristic of histon, and, on the other, the biuret reaction with sodium hydroxide and copper sulphate. Finally, the coagulability of the proteid was determined, the resulting coagulum being soluble in mineral acids.

It is therefore highly probable that the precipitate produced by acetic acid in this sample of urine is identical with nucleohiston.

J. F. T.

Chemistry of Vegetable Physiology and Agriculture.

The Changes which take place in Milk, either spontaneously or during Culinary Processes. By ANTOINE BÉCHAMP (*Bull. Soc. Chim.*, 1896, [4], **18**, 248—272. See this vol., ii, 113).—A continuation of a historical review of the subject. M. W. T.

Detection and Distribution of Glucase, the Enzyme of Maltose. By MARTINUS W. BEYERINCK (*Bied. Centr.*, 1896, **25**, 753—757; from *Centr. Bakt. Par.*, **1**, 2 Abt., 221, 265, and 329).—In this paper, the term amylase has been adopted for all the starch-decomposing enzymes, whilst those which simultaneously produce maltose and achroodextrin from starch are termed granulases.

The following methods, employed for the detection of these substances, depend on their power of diffusion. To detect the two amylases in barley, for instance, thin sections are placed on the surface of a solidified mixture of 10 per cent. gelatin solution with about 0·5 per cent. of potato starch; the maltase and granulase diffuse into the gelatin, producing, by amylolytic action, a visible circular field of diffusion. To determine the nature of the enzymes, the gelatin plate is treated with potassium iodide, when the diffusion field shows an inner, colourless zone, and an outer, reddish-violet zone, the rest of the gelatin

being blue. Maltose diffuses more quickly than granulase, and as the former produces (besides maltose) erythrodextrin, and the latter achroodextrin, the appearance of the gelatin plate as described is explained.

Another method is given which depends on the fact that microbes are very selective as regards certain nutritive substances, especially sugars. By means of a suitable substratum used in plate cultivations, the production of a particular sugar in consequence of amylolytic action is at once indicated by the growth of previously inoculated microbes. *Sacch. spiculatus* was found to be suitable, since it assimilates glucose but not maltose and dextrin.

According to Wysman, malt amylase consists of maltase and dextrinase. The latter is now shown to be a product of the action of heat on malt amylase. It is proposed to name the second enzyme, which occurs naturally in barley, granulase. The progressive destruction of the starch molecule is shown in the following table, in which the signs + and − indicate respectively that the substance in question is produced, or not produced, by the action of the amylase.

	From starch granulose				From erythrodextrin			From maltodextrin		From Maltose
	Erythrodextrin	Maltodextrin	Maltose	Glucose	Maltodextrin	Maltose	Glucose	Maltose	Glucose.	
1. Glucase	−	+*	+*	+	+*	+	+	+*	+	+
2. Maltase	+*	−	+	−	−	+	−	+	−	−
3. Granulase	−	+*	+	−	+*	+	−	+	−	−

Only the products formed in the breaking up of starch granulose are included in the table, as the other substances formed are not suitable for characterising the amylases.

Glucase does not seem to be widely distributed in plants and animals; sorghum contains a good deal, rice less, barley, wheat and rye only traces. It was not found in ordinary grass, but could readily be detected in maize leaves. Most seeds with mealy endosperm, belonging to the dicotyledons, contain maltase and glycase, whilst granulase is only produced during germination. As regards animal juices and organs, the liver alone was found to contain much glycase. It seems, however, to be widely distributed among the mould fungi.

N. H. J. M.

Enzyme Action. By G. HARRIS MORRIS (*J. Fed. Inst. Brewing*, 1896, **2**, 350—361).—A brief historical account of the various enzymes at present known and their mode of action is given, after which the author describes in detail his experiments on the hydrolytic action of yeast on maltose (Proc., 1895, 46). The recently published results of Fischer (Abstr., 1895, 441) are confirmed, and the following additional observations are recorded. No conversion of maltose into dextrose occurred in the presence of an alcoholic solution of thymol, 25 per cent. alcohol, or a half-saturated aqueous solution of ether. The hydrolysis of maltose by moist yeast is now known, therefore, to take place in the presence of toluene, thymol, or a saturated aqueous solution of ether, but not in the presence of the first-mentioned series of substances or of chloroform, or when the digestion is effected in the absence of any antiseptic. It is ex-

* Intermediate products which undergo further change.

tremely probable that the fermentation of maltose is accompanied by its hydrolysis, the two changes taking place practically simultaneously. The author fails to find any evidence of the existence of a maltose-hydrolysing enzyme in malt. A. C. C.

Transpiration of the Potato. By POLJANEC (*Bied. Centr.*, 1896, **25**, 786; from *Oesterr. bot. Zeit.*, 1895).—The daily transpiration of unpeeled potatoes as compared with tubers which had been half-peeled (that is, freed from dead periderm), and with tubers which had been completely peeled, was found to be as 1 : 4 : 200. The results show the great power of the periderm in checking transpiration, and also that the suberised cells, especially of newer organs, allow the passage of water vapour. The numbers given do not apply generally, as transpiration is influenced by variety. N. H. J. M.

Fruit of Myroxolon Pereiræ and of White Peru Balsam. By H. GERMANN (*Arch. Pharm.*, 1896, **234**, 641—647).—The seeds of *Myroxolon Pereiræ* often exhibit on their surface well-developed crystals of coumarin, which apparently does not occur in the interior of the seed. The fats which are present consist of palmitin, stearin, and olein. The finely powdered shells of the seeds were extracted first with hot alcohol, and then with ether; the hot alcoholic solution, on cooling, yielded *myroxocercin*, $C_{12}H_{20}O$, a reddish powder of indifferent nature. The alcoholic solution, on distillation, left a residue from which boiling water extracted a tannin and glucose. Part of the residue insoluble in water dissolved in 1 per cent. potash, but was precipitated again on the addition of concentrated potash. After several recrystallisations from alcohol, a pure compound *myroxofluorin*, $C_{42}H_{64}O_{10}$, was obtained.

Myroxol, $C_{46}H_{68}O_{10}$, a substance of alcoholic nature, and *myroxoresen*, $(C_7H_{10}O)_n$, were also isolated; the latter is not decomposed by fusion with potash, and after prolonged treatment with concentrated nitric acid yields picric acid.

The ethereal extract yielded a substance *myroxin*, $C_{23}H_{36}O$.

The author has also investigated two specimens of balsam from the fruits of Peru balsam trees. J. J. S.

The Tannin of Hops. By JOHN HERON (*J. Fed. Inst. Brewing*, 1896, **2**, 162—180).—The author considers Löwenthal's method by far the most accurate for the estimation of tannin in hops. Experiments are recorded showing the disappearance of tannin which occurs during the storage of hops. One sample, which in 1883 contained 6·2 per cent. of tannin, in 1891 contained only 1·3 per cent. In some cases, after the lapse of four years the tannin had entirely disappeared.

It is probable that phlobaphen (the condensation product of hop tannin described by Etti) is first formed, and that this undergoes oxidation to some substance allied to gallic acid, and that finally compounds are formed which are not acted on by the potassium permanganate solution employed in the determination. The greater part of the change takes place during the first year of storage. Hops which have been sulphured on the poles do not deteriorate so rapidly in this respect as those which have not been so treated. The author finds that, contrary to general opinion, the hop tannin does not cause the precipitation of proteid sub-

stances from the wort during the boiling in the copper, but is of opinion that combination between certain nitrogenous constituents of the wort and the tannin occurs, resulting in the formation of a soluble substance, *tanno-peptone,* which is readily soluble in solutions of organic acids, and which resembles peptone in its general properties. Samples of hops rich in tannin were also found to be rich in those resins and bitter substances which are of value to the brewer. A. C. C.

Occurrence of Cytisine in different Papilionaceæ. By PIETER C. PLUGGE and A. RAUWERDA (*Arch. Pharm.*, 1896, **234**, 685—697. Compare Abstr., 1896, ii, 61.)—The authors have examined the seeds of the plants previously enumerated, together with a number of others, for cytisine. The alkaloid was tested for by the method recommended by Van de Moer, by means of ferric chloride (5 per cent. solution) and hydrogen peroxide (0·05 per cent. solution). Cytisine has been found in the following 23 species belonging to this order, in addition to those already mentioned (*loc. cit.*). *Cytisus Attleanus, C. candicans* (Lam.), *C. formosissimus, C. monspessulanus* (L.), *C. ponticus, C. ruthenicus* (Fisch.), *C. scoparius* (Link.), *Ulex hibernicus* (G. Don.), *U. Jussiæi* (Webb), *U. parviflorus* (Pourr.), *Genista ephedroïdes* (D. C.), *G. florida, G. monosperma, Sophora flavescens, S. sericea, S. angustifolia, Baptisia alba, B. bracteata, B. exalata, B. leucantha, B. minor, B. perfoliata,* and *B. versicolor.*

Cytisin, however, could not be identified in *Cytisus æolicus* (Guss.), *C. canescens, C. Everestianus* (Carr), *C. falcatus* (Waldst and Kit.), *C. pullulans* (Kit.), *C. purpureus* (Scop.), *C. racemosus* (Hort), *C. ramosissimus, C. Rochelii* (Wiersb.), *C. serotinus* (Kit.), *C. sessiliflorus* (Poir.), *C. triflorus* (l'Herit.), *Genista Andreana, G. canariensis, Sophora alata, S. alopecuroïdes, Baptisia leucophæa, Coronilla Emerus, C. glauca, Robinia pseudacacia* (L.), *Wistaria sinensis* (Nutt.), *Albizzia stipulata, Amorpha fructicosa* (L.), *Anthyllis tetraphylla* (L.), *Arthrolobium scorpoïdes, Caragana arborescens, Desmodium canescens* (D. C.), *Gleditschia sinensis, G. triacanthos, Kennedya rubicunda, Psoralia capitata,* and *Tetragonolobus purpureus.* J. J. S.

Phosphoric Acid in Barley and Malt. By AUG. FERNBACH (*J. Fed. Inst. Brewing,* 1896, **2**, 128—140).—The author has made estimations of the percentages of soluble and insoluble phosphoric acid in a number of samples of barley, and in the malts prepared from them, with the object of ascertaining the nature of the changes taking place in the phosphates of the grain during the malting process. He finds that, in eight samples out of nine, a considerable proportion of the insoluble phosphates is rendered soluble, and that the percentages of soluble phosphoric acid (calculated on the total phosphoric acid) are much more uniform in the malts than in the barleys. At the same time, the percentage of total phosphoric acid is reduced. In the ninth sample experimented with, there was a diminution of the soluble phosphates, due to the fact that the original barley contained almost the whole of its phosphoric acid in the soluble state, and that a very hard water was employed for steeping, the phosphoric acid being therefore precipitated, as insoluble phosphates. It is suggested that organic acids produced during germination react with the insoluble dibasic and tribasic phosphates, converting them into soluble acid phosphates. Malt infusions always require the addition of small quantities of acid in order to render them neutral

to methyl-orange, and of small quantities of alkali to render them neutral to phenolphthalein, from which it is inferred that such infusions contain no free acids, but only acid salts, chiefly phosphates. A table is given showing the results of such titrations in the case of twelve samples of malt. Free acid is found to exercise a distinctly retarding effect on the saccharification of starch by diastase, whilst the acid phosphates exert no such unfavourable action. A. C. C.

[NOTE BY ABSTRACTOR.]—Brown and Morris have found that small quantities of lactic and other free acids distinctly favour the action of diastase on starch.

Swedish Fodder Plants. By A. G. KELLGREN and LARS F. NILSON (*Bied. Centr.*, 1896, **25**, 732—736; from *Kgl. landtbruks-akad.*, No. 31 1895, 1—93; comp. *Bied. Centr.*, 1894, **23**, 249, and Abstr., 1893, ii, 592).—The plants examined were all collected near the river Lule at the arctic circle. The vegetation was strongest close to the river, where *Carex acuta*, and especially *C. aquatilis*, which grew to the height of about 5 feet, were found. At some distance from the river, the predominant vegetation consisted of *C. ampullacea Goodeenovii* and *vesicaria*, besides some varieties of *Eriophorum* and *Juncus*, whilst the marshy land beyond is covered with herbage, including those varieties already mentioned and a number of others besides.

The following average results are given (per cent. of dry substance). 1. *Gramineæ*. 2. *Cyperaceæ*. 3. *Juncaceæ*. 4. Miscellaneous herbage. 5. Trees and bushes (*Arctostaphylus alpina*, *Betula odonta*, *Salix herbacea*). 6. *Equisetaceæ*. 7. Lichens (*Alectoria jubata*).

	Total nitrogen.	Ether extract.	Cellulose.	N free extract.	Digestibility co-efficient of nitrogen.	Amide nitrogen.	Ash.
1.	1·54	1·86	34·02	48·67	77·0	0·27	5·85
2.	2·27	2·28	26·68	50·59	59·8	0·39	6·27
3.	1·72	1·99	26·25	55·73	57·5	0·27	5·29
4.	2·41	2·47	22·37	50·84	76·7	0·32	9·25
5.	2·70	4·41	12·10	62·62	56·9	0·17	3·97
6.	2·67	2·29	17·17	47·77	82·6	0·53	16·10
7.	0·75	0·99	1·17	91·54	29·4	0·13	1·49

The much greater food value found for the *Cyperaceæ* (2) as compared with the *Gramineæ* (1), is in accordance with the preference shown by the inhabitants for the former. With regard to trees and bushes (5), large quantities of leaves (especially birch leaves) are used in many parts of the country, and the plants examined probably form an essential portion of the winter food of reindeer. *Equisetum fluviatile*, as green fodder, is said to be favourable to milk production; it is also made into hay. *E. palustre* and *E. arvense* are used for feeding horses and cows respectively. N. H. J. M.

Analyses of Norwegian Hay. By FR. WERENSKIOLD (*Bied. Centr.*, 1896, **25**, 736—737; from *Tidsskr. Norsk. Landbr.*, 1896, **3**, 328—332. Compare Abstr., 1895, ii, 324).—The results of new experiments show that the composition and digestibility of different samples of the same plant vary considerably. There seems, however, to be a distinct

difference between *Leguminosæ* and grasses. The following percentage results were obtained with different kinds of hay.

		Crude proteids.	Digestible proteids.	Indigestible proteids.	Amides.	Coefficient of digestibility of crude proteids.	Coefficient of digestibility of proteids.
Trifolium pratense		11·38	2·28	5·04	4·06	55·7	31·1
,, *hybridum*		11·38	2·55	4·21	4·62	63·0	36·2
Anthyllis vulneraria		11·52	4·03	3·15	4·34	72·7	56·2
19 Grasses	Max.	6·10	2·75	2·69	2·57	79·4	—
	Min.	3·08	0·87	0·44	0·62	55·9	—

A sample of *Astragalus Oroboides* (collected 13th July) furnished hay containing 24·38 per cent. of crude proteids; the digestibility coefficient was 86·5. The percentage of indigestible proteids was 3·30, digestible proteids 10·04, and amides 11·04. N. H. J. M.

Examination of Linseed Meal. By Fritz W. A. Woll (*Ann. Rep. Agr. Exp. Stat. Wisconsin* for 1895, **12**, 64—85).—Linseed cake prepared by the old method, in which the moistened seeds were heated to about 70—80° and pressed, contained 6—7 per cent. of fat. In the new method, the crushed and heated seeds are extracted about 12 times with light petroleum, and the seeds, after being steamed to remove the light petroleum, are dried and ground. The meal so obtained contains fat (3·2 per cent.) and proteids (37·9 per cent.), whilst by the old method it contained 7·2 and 35·9 per cent. of fat and proteids respectively. The proteids are abnormally high owing to the climatic conditions of 1894. The lower digestibility of the residues extracted with light petroleum is attributed to the steaming.

The two kinds of meal can be distinguished by means of the "swelling test" in the following manner. The meal (5 grams) is mixed with boiling water (50 c.c.) in a graduated cylinder and left for 2 hours, and the amount of clear liquid read off. Whilst meals prepared by the old process absorb the whole of the water added, those obtained after extraction with light petroleum only absorbed from 4·1 to 6·3 parts. As regards the feeding value of the meal, the percentage of fat and proteids are, of course, more important than the absorptive power for water. The method is, however, very useful for ascertaining the process by which the meal was made. N. H. J. M.

Analytical Chemistry.

Table of Factors. By EDMUND H. MILLER and J. A. MATHEWS (*J. Amer. Chem. Soc.*, 1896, **18**, 903—904).—A convenient table for the conversion of the weights of precipitates of constant composition into the corresponding metal or oxide, or acid radicle. The logarithm is given in each case. L. DE K.

Convenient form of Measuring-flask. By WILHELM WISLICENUS (*Ber.*, 1897, **30**, 278. Compare this vol., ii, 70).—The flask described

by the author (*loc. cit.*) has been already introduced by Biltz (Abstr., 1896, ii, 671) and by Giles (Abstr., 1894, ii, 251). M. O. F.

Some Extensions of the Plaster of Paris Method in Blowpipe Analysis. By W. W. Andrews (*J. Amer. Chem. Soc.*, 1896, **18**, 849—869).—The author has improved this well-known process by introducing a set of new reagents and by improving the material. A solution of iodine in potassium thiocyanate is now used to produce volatile iodides in place of hydriodic acid, whilst a mixture of potassium bromide and potassium hydrogen sulphate or phosphate is substituted for fuming hydrobromic acid. A mixture of potassium chloride, iodide, or fluoride with metaphosphoric acid is also found to be a useful reagent. To dissolve the films, the author now employs potassium cyanide solution rendered more stable by the addition of a little free alkali, whilst a solution prepared by boiling aqueous potash with excess of flowers of sulphur is substituted for yellow ammonium sulphide in order to dissolve the films and produce sulphide spots.

In order to produce coloured fluxes on the tablets, the material must be made more resistant to the dissolving effect of the metaphosphoric acid and of the alkali in the borax. The author advises adding a teaspoonful of boric acid to every quart of water used in making the plaster tablets.

The great delicacy of the plaster blowpipe assay is again proved by numerous instances. L. de K.

Effect of an Excess of Reagent in the Precipitation of Barium Sulphate. By C. W. Foulk (*J. Amer. Chem. Soc.*, 1896, **18**, 793—807).—The author has made a large number of experiments on the best way of precipitating barium sulphate, and tabulated the results.

It appears that when a barium salt is precipitated by sulphuric acid in the presence of hydrochloric acid, a large excess of the reagent is required, especially if the quantity of hydrochloric acid is very large. If the precipitate has to be collected at once, a very large excess of sulphuric acid should be added, as otherwise it would be necessary to leave the mixture for some time, stirring at intervals.

Barium sulphate obtained by the use of excess of sulphuric acid in the presence of hydrochloric acid is coarse and crystalline; that obtained by adding excess of barium chloride is finely divided and liable to run through the filter. The precipitation is not complete unless an excess of the reagent is added, particularly so if there is much hydrochloric acid present. The precipitate always contains occluded barium chloride which no amount of washing can remove; it may, however, be extracted from the precipitate after ignition by repeated treatment with boiling water and re-ignition. If the moist filter containing the precipitate is put into a platinum crucible, precipitate end up, and then gradually burnt, no reduction to sulphide takes place. L. de K.

Elementary Analysis under pressure in a Closed Vessel. By Walther Hempel (*Ber.*, 1897, **30**, 202—211).—The author proposes to carry out combustions of organic substances in compressed oxygen (25 kilos. to the square cm.) in a modified form of the Berthelot calorimetric bomb, which is made of such dimensions that it can be accurately

weighed (250 grams). After the combustion, which is carried out as in thermochemical determinations, the gases are allowed to escape slowly through the absorption tubes, and the bomb is then twice filled with pure air, and pumped out through the absorption tubes by means of a water pump. The amount of nitrous acid formed is determined by washing out the bomb (after it has been treated as above and weighed), with water, and titrating with centinormal alkali. Sulphur, if present, is entirely converted into sulphuric acid, which is estimated in the usual way. The amount of water formed is given by the increase in weight of the calcium chloride and sulphuric acid tubes which are used *plus* the increase in weight of the autoclave, *minus* the weight of acids formed. As the apparatus has to be exhausted, soda lime tubes are used for absorbing the carbonic anhydride.

A. H.

Estimation of Arsenic, Antimony, and Foreign Metals in Commercial Copper by Electrolytic Methods. By A. HOLLARD (*Compt. rend.*, 1896, **123**, 1063—1065).—When hydrogen sulphide is passed through the liquid from which the copper has been electrolytically removed, the precipitate may contain arsenic, antimony, lead, and perhaps traces of copper, whilst iron, nickel, and cobalt may be present in the filtrate. The sulphides of arsenic and antimony are separated from the other sulphides by solution in ammonium sulphide, the arsenic being eventually precipitated as magnesium ammonium arsenate, and the antimony reprecipitated as sulphide, the latter being dissolved in concentrated sodium sulphide solution, and the antimony deposited by electrolysis. From the filtrate from the hydrogen sulphide precipitate, the iron is removed as hydroxide, the nickel and cobalt being deposited electrolytically from an ammoniacal solution containing ammonium sulphate.

Estimation of Silver.—If the copper is rich in silver, the whole of the latter will be deposited with the copper, but if the amount of silver is but small, then the silver, in from 10 to 50 grams of the metal, is precipitated as chloride, dissolved in 2 per cent. potassium cyanide solution, and submitted to a current of 0·025 to 0·035 amp.

Lead may be estimated by electrolysing a nitric acid solution of the copper, the platinum cone being connected with the positive, and the spiral with the negative pole. At the end of 12 hours, the lead is entirely deposited on the cone as hydrated peroxide. The intensity of the current should be 0·3 amp. A. C. C.

Estimation of Thoria. Analysis of Monazite Sand. By CHARLES GLASER (*J. Amer. Chem. Soc.*, 1896, **18**, 782—793).—Two grams of the finely pulverised mineral is heated with strong sulphuric acid, or fused with potassium hydrogen sulphate; on treating the fused mass with cold water, silica and tantalic acid are left undissolved, but must be freed from traces of thoria by repeated treatment with hydrofluoric and sulphuric acids; the thoria solution is then added to the main liquid. This is freed from titanium, &c., by treatment with hydrogen sulphide, first at the boiling heat and then in the cold. After filtering, the liquid is boiled to expel the gas, any excess of acid is neutralised with ammonia, and the thoria, together with other

metals of the cerium group, is precipitated by adding 100 c.c. of a saturated solution of ammonium oxalate previously heated to boiling.

The oxalates are next reduced to oxides by ignition, converted into sulphates, the greater part of the acid neutralised with ammonia, the solution heated to boiling, and hot ammonium oxalate solution added in excess; after a little while, a few c.c. of ammonium acetate is added. On cooling, the metals of the cerium group are precipitated as oxalates, leaving the thoria in solution; the latter can then be precipitated with ammonia, washed, ignited, and weighed.

The author also gives a detailed account of the estimation of titanic acid, tantalic acid, glucina, zirconia, and yttria, lanthanum and didymium oxides, cerium oxide, ferric oxide, lime, alumina, lead, silica, and phosphoric acid, all of which occur in the monazite sand.

L. DE K.

Estimation of Aluminium in Phosphates. By HENRI LASNE (*Bull. Soc. Chim.*, 1896, [4], **15**, 237—248).—The author has studied sources of error in the different methods of analysing phosphates containing alumina. Methods involving the precipitation of alumina as phosphate in presence of ammonium acetate give erroneous results, on account of the variation of the composition of the precipitate and of the solubility of the alumina. The latter increases with the amount of acetic acid present, and vanishes when the solution is slightly ammoniacal. The amount of phosphoric acid in the precipitate increases with the quantity present in the solution.

In the case of aluminium phosphate precipitated in the presence of ammonium thiosulphate, it was found that the quantity of phosphoric acid in the precipitate increased with the quantity present in the solution up to a certain point, and then became fairly constant. A correction could be made for the loss of alumina due to solubility if the conditions were kept constant.

A sample of known composition was analysed by several different methods, of which the oxalic acid method alone gave satisfactory results.

M. W. T.

Analysis of Aluminium. By JAMES O. HANDY (*J. Amer. Chem. Soc.*, 1896, **18**, 766—782).—The best solvent for commercial aluminium is a mixture of 100 c.c. of nitric acid of sp. gr. 1·42, 300 c.c. of hydrochloric acid of sp. gr. 1·20, and 600 c.c. of 25 per cent. sulphuric acid. One gram of aluminium borings is dissolved in 30 c.c. of the acid mixture, and the solution evaporated until dense fumes of sulphuric acid begin to appear; after cooling slightly, the residue is boiled with 100 c.c. of water and 10 c.c. of weak sulphuric acid, 1 gram of metallic zinc is added, and the whole heated for some time to precipitate the copper and reduce the iron to the ferrous state. The latter is then titrated with permanganate, whilst the copper, mixed with silica, is dissolved in dilute (15 per cent.) nitric acid, and titrated with potassium cyanide, after the addition of a slight excess of sodium carbonate. The undissolved silicon and silica are first fused with sodium carbonate, and afterwards recovered by evaporating with sulphuric acid; the result is finally calculated to silicon. Graphitic or crystalline silicon

may be estimated by dissolving 1 gram of the metal in 30 c.c. of dilute hydrochloric acid (1 : 2) in a platinum dish, and adding to the solution 2 c.c. of hydrofluoric acid, which dissolves the non-crystalline silicon, but does not attack the graphitic variety; after filtering, for which a funnel coated with paraffin must be used, the residue is ignited and fused with sodium carbonate and the silica estimated as directed above.

To estimate any sodium, 1 gram of the borings is dissolved in 50 c.c. of nitric acid with a sufficiency of hydrochloric acid; the solution is boiled to expel chlorine, evaporated in a platinum dish, and finally heated until no more nitric fumes are given off. The residue is then powdered, and treated as if it were an estimation of alkalis in a silicate, namely, by fusing with 1 gram of ammonium chloride and 8 grams of pure calcium carbonate, &c. Carbon and nitrogen are estimated by Moissan's method, slightly modified.

If it is desired to make a direct estimation of the aluminium, the following process is recommended. One gram of the sample is dissolved in 30 c.c. of dilute hydrochloric acid, evaporated to dryness, and the residue boiled with 10 c.c. of strong hydrochloric acid and 75 c.c. of water. After diluting to 250 c.c., hydrogen sulphide is passed through the solution, which is filtered, and the excess of hydrogen sulphide boiled off, the last traces being removed by adding 1 c.c. of strong nitric acid, and boiling for 10 minutes. When cold, the liquid is made up to 500 c.c., 50 c.c. is pipetted off, diluted to 250 c.c., heated to boiling, and a slight excess of ammonia added, the boiling being continued for 20 minutes. The alumina is collected, washed with boiling water, ignited, and weighed as quickly as possible, as, according to the author's experience, the precipitate is exceedingly hygroscopic.

The rest of the paper is devoted to the analysis of alloys of aluminium with copper, nickel, manganese, chromium, tungsten, titanium, zinc, tin, and phosphorus; also to the analysis of crude hydrated alumina and of bauxite, but, although containing useful details, the processes used, on the whole, present no novel features. L. DE K.

Analytical Methods involving the Use of Hydrogen Peroxide. By B. B. Ross (*J. Amer. Chem. Soc.*, 1896, **18**, 918—923).—Baumann has used hydrogen peroxide for the estimation of chromic acid and chromates; the latter, when mixed with a sufficiency of sulphuric acid and an excess of hydrogen peroxide, gives off 8 atoms of oxygen for every molecule of chromic acid, or 445·3 c.c. of oxygen for 1 gram of the acid.

The author, having repeated Baumann's experiments, has successfully applied the process to the indirect estimation of iron. After reducing the ferric compound to the ferrous state, an excess of standardised solution of potassium dichromate is added, and the undecomposed chromic acid is then estimated by means of hydrogen peroxide.

The author has tried to apply the process in sugar analysis. For this purpose, the sugar is inverted, and then boiled with alkaline copper tartrate solution; and the precipitated cuprous oxide, after being well washed, is boiled with dilute sulphuric acid and a known quantity of potassium dichromate, the excess of which is then estimated by the

hydrogen peroxide process. Although free from objection in theory, the practical results have, as yet, not been altogether satisfactory.

L. DE K.

Reducing Action of Chloroform on Fehling's Solution. By CHARLES G. MATTHEWS (*J. Fed. Inst. Brewing*, 1896, **2**, 333—334).—It is known that chloroform reduces Fehling's solution, and the author has made determinations of the amount of cupric oxide obtained by the ordinary gravimetric method, corresponding with known weights of chloroform. It is found that 1 c.c. of that substance gives 1·72 gram of cupric oxide, or that 1 gram gives 1·15 gram of cupric oxide. When, therefore, as is often the case, chloroform is added to a sugar solution which is to be analysed, it should be either expelled by boiling before the estimation of the sugar is undertaken, or its cupric-reducing power should be taken into account and a correction made. A. C. C.

Estimation of Alcohol. By H. DROOP RICHMOND (*J. Fed. Inst. Brewing*, 1896, **2**, 529—535).—In estimating the percentage of alcohol in a liquid indirectly, from the sp. gr. of the liquid itself and that of the non-volatile portion (extract) remaining after distillation, the sp. gr. of the distilled alcohol can be obtained, according to Tabarie, by dividing the sp. gr. of the liquid by that of the extract. It was subsequently pointed out by Blunt that more correct results were obtained if the sp. gr. of the extract (water = 1) were subtracted from that of the original liquid + 1. In this communication, the author demonstrates the theoretical accuracy of Blunt's method. A. C. C.

A New Method for the Estimation of Glycerol. By FRÉD BORDAS and SIG. DE RACZKOWSKI (*Compt. rend.*, 1896, **123**, 1071—1072). —The authors employ a slight modification of the process suggested by Nicloux for the estimation of small quantities of alcohol. A solution of potassium dichromate (48 grams per litre) is added to 5 c.c. of a dilute solution of glycerol containing 2 c.c. of sulphuric acid, until the dichromate is completely reduced, a very slight excess of the latter changing the colour of the liquid from a bluish-green to a yellowish-green. The glycerol solutions must not contain less than 0·1 gram or more than 2 grams per litre, since the colours are then either too faint or too intense. Every 1 c.c. of the above dichromate solution corresponds with 0·005 gram of glycerol. A. C. C.

Estimation of Reducing Sugars in Terms of Copper Oxide. By GEORGE DEFREN (*J. Amer. Chem. Soc.*, 1896, **18**, 749—766).—The author has reinvestigated the relation between copper oxide and anhydrous dextrose, maltose, and lactose, and has tabulated the results, the method employed being the same as that recommended by O'Sullivan (this Journal, 1876, ii, 130). The dextrose equivalent varied from 0·4401 to 0·4511; that of maltose from 0·7240 to 0·7433 and that of lactose from 0·6289 to 0·6430.

These differences are due to the influence of dilution, the equivalent becoming greater as the solution employed is more concentrated. The author has constructed a very useful and complete table for the benefit of sugar analysts, giving the empirical relation between percentage of

copper oxide obtained and the corresponding dextrose, maltose, and lactose. L. DE K.

Estimation of the Ready-formed Sugars of Malt. By G. HARRIS MORRIS (*J. Fed. Inst. Brewing*, 1896, **2**, 224—237).—The method usually employed for the estimation of the ready-formed sugars of malt, consists in making a cold water extract of the malt, and then estimating the amount of total dissolved solid matter. From this number, the sum of the percentages of the soluble uncoagulable proteids, the ash, and the acid is subtracted, the difference being taken as representing the ready-formed sugars. The author has endeavoured to determine these sugars directly, both by fermentation and by ascertaining their cupric oxide reducing power, and expressing the results in terms of dextrose. He finds, however, that both of these methods give inaccurate results, and that the older method yields numbers which bear a fairly constant relation to the true sugars, as determined by the alcohol extraction method of C. O'Sullivan (Trans., 1886, 58). The following conclusions bearing on the above method are recorded. When ground malt is digested with water at 60°F., no diastatic action takes place during the first 3 hours. After this period, the starch granules are acted on, maltose being formed. At higher temperatures, diastatic action is more marked, although not very considerable, between 60°F. and 70°F. The more tender the malt, the greater is effect of temperature on this action. A. C. C.

Invert-Sugar, I, II. By JOHN HERON (*J. Fed. Inst. Brewing*, 1896, **2**, 440—452, 457—482).—In Part I of this communication, a detailed account is given of the manufacture of invert-sugar, together with typical analyses of raw cane-sugar, and of invert-sugar.

In the second part, methods for the analysis of the commercial products are described which are considered by the author to give the most accurate results. A 1 per cent. solution of the mineral matter contained in such samples has, approximately, a sp. gr. = 1·008. In the estimation of the total organic solid matter in samples of sugar by the use of the 3·86 divisor, it is necessary, therefore, to estimate the amount of ash, and then to correct for its influence on the specific gravity of the solution. A. C. C.

Composition and Fermentability of Fruit-sugar. By KELHOFER (*Bied. Centr.*, 1896, **25**, 760—761; from *Jahresber. Versuchs-Stat. Wädensweil*, 1895, **4**, 93).—The original preparation known as fruit-sugar was a yellowish syrup containing 75 per cent. of sugar (dextrose and levulose), and therefore a suitable substitute for natural fruit-sugar. A substance similar in appearance to this, and containing the same amount of sugar, is now made, but the sugar consists of, for example, 39·45 percent. of invert-sugar and 34·75 percent. of cane-sugar. The more recent preparation, apart from being in the form of a syrup, has no advantage, when its greater cost is considered, over cane-sugar, either for effervescent liquids, food for bees, or as regards fermentability. N. H. J. M.

Acidity of Milk increased by Boric Acid. By E. H. FARRINGTON (*J. Amer. Chem. Soc.*, 1896, **18**, 847).—The author has found that a

solution of boric acid in milk, shows about 4 times as much acidity as when the same amount of the acid is dissolved in water.

If, therefore, milk shows a high acidity, and is still fairly neutral to the taste, it may be safely assumed to contain boric acid.

L. DE K.

Behaviour of the Resin Acids of Shellac in Gladding's and Twitchell's Processes for separating Fatty and Resin Acids.—By FERDINAND ULZER and RUDOLF DEFRIS (*Zeit. anal. Chem.*, 1897, **36**, 24—27).—The resin acids of shellac behave, in Gladding's process (Abstr., 1882, 663), more like fatty acids than like those of pine resin, their silver salts being for the most part insoluble in ether. A dark sample of shellac, with the acid number 65·43, saponification number 204·78, and only 0·05 per cent. of unsaponifiable constituents, furnished 12·9 per cent. of "resin acid" by this method. Twitchell's process (Abstr., 1892, 389) consists in passing gaseous hydrogen chloride into an alcoholic solution of the acids, when fatty acids are converted into their ethylic salts, whilst resin acids remain free. After removal of the alcoholic hydrogen chloride by washing with water, the ethereal layer is dissolved in light petroleum and this solution shaken with soda, when the resin acids saponify. The above sample of shellac treated by this method yielded 66·56 per cent. of "resin acid," but at the same time a certain amount of an ethereal salt was produced having the saponification number 199·5. A second specimen yielded 72·89 per cent. of "resin acid."

M. J. S.

Estimation of Fats, Soaps, and Fatty Acids in Animal Organs. By CARL DORMEYER. (*Pfluger's Archiv*, 1896, **65**, 90—108. Compare, Abstr., 1895, ii, 540).—Renewed experiments confirm the author's previous conclusion that simple extraction of animal organs with ether is useless as a trustworthy method of estimating fats, soaps, fatty acids, or cholesterol. Even after a month's extraction, much fat remains undissolved. But after preliminary artificial gastric digestion, an additional amount of fat is extractable, averaging 8·5 per cent. of the total quantity.

W. D. H.

Estimation of Free Fat in Soap. By WM. WALTKE (*Chem. Zeit.*, 1896, **20**, 38).—Ten grams of the thoroughly dried sample is powdered in a mortar, introduced into a graduated 200 c.c. tube, and shaken with 100 c.c. of light petroleum free from moisture and non-volatile matters. The liquid is then poured off from the deposit through a filter, and 50 c.c. of the filtrate is evaporated in a weighed platinum dish, the residue being finally dried at 110°. The fat, should the least trace of moisture have been present, may contain some soap; to ascertain whether this is the case, it must be dissolved in a little light petroleum, when, if free from soap, it will yield a perfectly clear solution.

L. DE K.

Estimation of the Percentage of Alkali and Fatty Acids in Soap. By WM. WALTKE (*Chem. Zeit.*, 1896, **20**, 240).—A solution of 20 grams of the sample in about 100 c.c. of water, contained in a porcelain basin, is mixed with 70 c.c. of normal sulphuric acid, and heated until the fatty acids have completely melted. The

mixture is then cooled a little and rinsed by means of light petroleum into a 300 c.c. cylinder graduated to 0·25 c.c., and provided with a ground stopper, and a tap at the bottom. The aqueous layer should not occupy more than 200 c.c., and the petroleum layer not more than 100 c.c. After thoroughly shaking, the exact volumes of the two layers are carefully noted, and one-half of the top layer is pipetted off; after distilling off the light petroleum, the fatty acids are dried at 110° and weighed. The aqueous layer is now run off and the excess of acid titrated with normal soda. The amount of alkali in the soap is then easily calculated.

In some cases, where the use of light petroleum is inconvenient, on account of an emulsion being formed, the author employs either chloroform or carbon bisulphide; the aqueous layer then, of course, floats on the top. L. DE K.

Estimation of Fibrin in Blood. By A. KOSSLER and F. W. THEODOR C. PFEIFFER (*Zeit. anal. Chem.*, 1897, **36**, 70—71; from *Centr. inn. Med.*, 1896, 8.)—The method depends on the estimation of the nitrogen in equal volumes of the uncoagulated plasma and the defibrinated serum. The blood as it flows from the vein is mixed with about $\frac{1}{19}$th of its volume of a 4 per cent. potassium oxalate solution, and is then freed from blood corpuscles by centrifugal action. The nitrogen is estimated in a measured volume by Kjeldahl's process; another portion (20 c.c.) is caused to coagulate by the addition of 5 c.c. of a 2 per cent. calcium chloride solution. After some hours, the serum is pressed out from the clot with a glass rod, and when, by remaining liquid, it indicates that coagulation has ceased, it also is submitted to Kjeldahl's process. The result is multiplied by 25/20, to compensate for the dilution by the calcium chloride, and the difference between the two nitrogen determinations gives the fibrin nitrogen of the oxalate plasma. That of the original plasma is ascertained by Bleibtreu's method (Abstr., 1893, ii, 331; 1895, ii, 122). M. J. S.

Detection of Glucase, the Enzyme of Maltose. By MARTINUS W. BEYERINCK (*Bied. Centr.*, 1896, **25**, 753—757).—See this vol., ii, 183.

Estimation of the Diastatic Capacity of Malt. By ARTHUR R. LING (*J. Fed. Inst. Brewing*, 1896, **2**, 335—343). The method proposed by the author is a modification of Lintner's well-known method. Those tubes in the series in which the reduction is nearly complete are taken, and the amount of unreduced copper is determined by titration with a standard solution of dextrose containing 2 grams per litre. The exact number representing the diastatic capacity of the malt is thus more easily obtained than by making a second series of experiments with smaller quantities of the cold-water extract of malt. Satisfactory test-determinations are given. A. C. C.

General and Physical Chemistry.

Change of the Refractive Index by the Neutralisation, the Formation, and the Dilution of Solutions. By GUSTAV TAMMANN (*Zeit. physikal. Chem.*, 1896, **21**, 537—544).—The author endeavoured to determine whether the changes in the refractive index during the neutralisation of solutions are due to the changes in internal pressure, as it had been already proved that changes in volume and specific heat can be so explained (Abstr., 1895, ii, 204; 1896, ii, 289). The author deduces first the relation $\Delta n/\Delta v = -(n-1)$, where n is the index of refraction, and Δn and Δv are the refraction and volume changes resulting from alteration of pressure. This relation is in accordance with the determinations of Hallwachs for changes in n due to concentration changes, and with those of Pulfrichs on the formation of solutions. Electrolytic dissociation does not, however, as a rule, cause any change in the refractive index, except in the case of compounds containing hydrogen or hydroxyl ions. In these, the equivalent refraction of hydrogen increases by 1·8 on ionisation, and that of hydroxyl by 0·7, whilst the formation of ammonium from ammonia and a hydrogen ion is attended by an increase of 3·2 in the equivalent refraction.

L. M. J.

Atomic Refractions of Carbon, Hydrogen, Oxygen, and the Halogens. By ISIDOR TRAUBE (*Ber.*, 1897, **30**, 39—42).—The atomic refractions calculated by Brühl for the $(\mu^2-1)/(\mu^2+2)$ formula are all higher than the true values, as no regard was paid to the influence of association of the molecules in the case of certain liquids, this influence being more especially marked in the case of the first members of the different series of homologous compounds. Omitting all cases in which association is known or suspected to occur, and recalculating Brühl's values, the numbers obtained are found to agree closely with those calculated by the author from the molecular volumes (this vol., ii, p. 85). In the following table, the atomic refractions for the D line are given, the numbers in the first column being those obtained from the molecular volumes, and those in the second column Brühl's corrected numbers.

C	2·88	2·70	Cl	6·11	6·04
H	0·905	0·99	Br	8·85	8·84
O′	1·60	1·52	I	13·84	13·82
O″	,,	1·97	F	1·41	1·50
O_2	,,	1·58	F̶	1·60	1·83

The corresponding numbers for the $\mu-1$ formula may be obtained by multiplying the above by 1·659.

H. C.

Atomic Refractions of Nitrogen. By ISIDOR TRAUBE (*Ber.*, 1897, **30**, 43—47).—The author, in continuation of his work on the atomic refractions of the elements (see preceding abstract), has calculated from the molecular volume formula the atomic refraction of nitrogen in a large

number of nitrogen compounds. The atomic refraction of trivalent nitrogen in the amines, nitriles, and similar compounds is always the same, the mean value for the D line being 2·65. Nitrogen in the nitro-, nitroso-, azo-, oximido-, isocyanic, and ammonium compounds has a much higher atomic refraction, the mean value being 3·77. As the pentad nitrogen atom has a greater refraction than trivalent nitrogen, it may be that in these latter compounds the nitrogen is in every instance quinquivalent.

H. C.

Spectrometric Determinations. By JULIUS W. BRÜHL (*Ber.*, 1897, **30**, 158—162).—The author has directly determined the refractions of several organic compounds, and gives the following values for the molecular refractions for the H_α and Na lines calculated from the $(n^2-1)/(n^2+2)$ formula, and for the molecular dispersions $H_\gamma - H_\alpha$.

	H_α	Na	$H_\gamma - H_\alpha$
Ethylic ether, Et_2O	22·31	22·41	0·53
Methylal, $CH_2(OEt)_2$	19·08	19·16	0·43
Ethylic orthoformate, $CH(OEt)_3$	39·14	39·30	0·89
Ethylic orthocarbonate, $C(OEt)_4$	49·69	49·89	1·09
Hydrazine, $NH_2{\cdot}NH_2$	8·82	8·87	0·27
Dimethylhydrazine, $NMe_2{\cdot}NH_2$	18·58	18·68	0·60
Butylmethylamine, $NHMe{\cdot}C_4H_9$	28·61	28·76	0·76
Butylmethylhydrazine, $NH_2{\cdot}NMe{\cdot}C_4H_9$	32·32	32·50	0·92

H. C.

Hydrazine, Hydrogen Peroxide, Water. By JULIUS W. BRÜHL (*Ber.*, 1897, **30**, 162—172).—The author has in a former paper (Abstr., 1896, ii, 162) advanced the view that oxygen in hydrogen peroxide and water is quadrivalent, and that the former compound has the constitution HO⁚OH. It is here shown that compounds of the type $R_2N{\cdot}NH_2$ and $R_2N{\cdot}OH$, in which R may be any radicle or hydrogen, do not behave like hydrogen peroxide. The molecular refractions of compounds of this type are found to be equal to the sum of the refractions of their constituents, whereas in the case of hydrogen peroxide this is not so, the observed refraction being much greater than that calculated.

H. C.

Normal Rotatory Dispersions. By PHILIPPE A. GUYE and P. A. MELIKIAN (*Compt. rend.*, 1896, **123**, 1291—1293).—The authors have determined the rotatory dispersions of a number of carbon compounds; the specific rotatory powers for the line D, and the specific rotatory dispersions, are given in the following table. With the possible exception of methylic lactate, all the liquids are composed of simple molecules, and all have normal rotatory dispersion.

	Sp. gr.	t	$[\alpha]_D$	$[\alpha]_{V-Z}$
Propylene oxide	0·820	23·5°	+1·10	+1·02
Propylic β-methyladipate	0·978	16·5	+2·19	+2·39
Ethylic β-methyladipate	0·986	18	+2·25	+2·70
Isobutylic β-methyladipate	0·950	18	+3·01	+3·73
Secondary amylic chloride	0·851	23	+3·13	+3·32
Phenylamylic oxide	0·924	24	+3·62	+4·14

	Sp. gr.	t	$[\alpha]_D$	$[\alpha]_{V-Z}$
Methylic β-methyladipate	1·050	17°	+3·64	+3·16
Methylic 2 : 6-methyl-3-octanonate	0·950	16	+3·83	,,
Isopropylic β-methyladipate	1·034	16	+6·54	+4·99
Methylic lactate	1·080	16	−7·95	−4·33
Methylic butyryllactate	1·019	20	−38·68	−28·65
Methylic acetyllactate	1·080	15	−48·60	−36·97

Although the specific rotatory dispersions are of the same order of magnitude as the specific rotatory powers, they are not proportional tc them. C. H. B.

Spectra of Argon. By JOHN TROWBRIDGE and THEODORE W. RICHARDS (*Amer. J. Sci.*, 1897, [iv], **3**, 15—20; also *Phil. Mag.*, **43**, 77—83).—The present paper is preliminary to a more exhaustive study of the discharges of electricity through rarefied gases, by means of a storage battery of 10,000 cells, which will give an electromotive force of about 20,000 volts. The red glow of argon is readily obtained with a voltage of about 2,000, but not with much less; Crookes' estimate of 27,600 volts is evidently excessive. The introduction of a condenser between the terminals of the Geissler tube made no difference in the red glow as long as the connections were good and the condenser quiet. As soon as a spark gap was introduced, or the condenser began to emit the humming sound peculiar to it, the beautiful blue glow so characteristic of argon immediately appeared. If this light is examined by a revolving mirror, it is seen to consist of intermittent discharges. The battery charges the condenser to the potential necessary to produce a spark between the terminals of the spark gap; the discharge of this accumulated electricity is produced in the tube, and then the operation is repeated. The potential required certainly cannot be greater than 2,000 volts, the E.M.F. of the battery which will easily produce the blue glow.

The oscillatory discharge of the condenser is an important factor in producing the blue spectrum of argon, and the effect of the oscillatory discharge in producing the blue spectrum can also be shown by the use of an electrical machine. If the terminals of the tube containing argon are connected with the terminals of an electrical machine, the pure red spectrum is obtained. If a spark gap is interposed in such a manner that a condenser charged by the machine can discharge through the tube, the blue discharge immediately occurs; the condenser discharge oscillates through the gas.

When the tube containing argon at a suitable pressure is brought near a Hertz oscillator, giving a rate of about 115,000,000 oscillations per second, it immediately shows the blue colour. The unusual sensitiveness of an argon tube to oscillatory discharges indicates that it will be of great use in the study of wave-motions of electricity. The change of colour in the tube from red to blue is so marked that an argon tube reveals what is not shown in a conspicuous manner by other gases. The authors propose to call an argon tube fitted for the study of electrical waves a talantoscope. H. C.

Multiple Spectra of Gases. By JOHN TROWBRIDGE and THEODORE W. RICHARDS (*Amer. J. Sci.*, 1897, [iv], **3**, 117—120; also *Phil. Mag.*, **43**, 135—139).—Having shown (preceding abstract) that the con-

tinuous discharge of a high tension accumulator through argon produces the red spectrum, whilst the oscillatory discharge of a condenser produces the blue spectrum, the authors proceeded to determine whether the different spectra noticed in the case of other gases are primarily dependent on the electrical conditions which cause the gas to glow. With nitrogen, the two different spectra were obtained by varying suitably the electrical conditions of the discharge. With the continuous discharge, the channelled spectrum was obtained, but when the condenser was introduced, the channelled spectrum gave place to bright lines, already well known and mapped. This line spectrum corresponds with the blue spectrum of argon. Hydrogen under the influence of the continuous discharge gives a multitude of sharp lines, among which the four usual hydrogen lines, although present, are by no means especially prominent. A large capacity is required to change this spectrum into the familiar four-line spectrum which is comparable with the blue spectrum of argon. Each of the halogens gives two spectra, one with and one without the condenser. Helium gave a brilliant yellow glow under the influence of the continuous discharge, and a brilliant blue with the condenser discharge, but since the bright helium lines remained in each, and every other important line in the blue spectrum proved to be an argon line, it is evident that the oscillations produced no considerable effect on the helium. H. C.

Potential Differences between Metals and Electrolytes. By OTTO WIEDEBURG (*Ann. Phys. Chem.*, 1896, [ii], **59**, 742—749).—A theoretical paper dealing with the determination of contact differences of potential between metals and electrolytes, and in answer to objections to the Lippmann-Helmholtz theory of capillary electrical phenomena. H. C.

Experimental Investigations on the Electrolysis of Water. By ALEXEI P. SOKOLOFF (*Ann. Phys. Chem.*, 1896, [ii], **59**, 802—804).—Corrections to some of the tables in the author's former communication on this subject (Abstr., 1896, ii, 510). H. C.

Electrolytic Behaviour of Solutions of some Salts and Acids in Methylic Alcohol. By GIACOMO CARRARA (*Zeit. physikal. Chem.*, 1896, **21**, 680).—In the communication by Zelinsky and Krapiwin (this vol., ii, 5) on the above subject, reference was omitted to the author's work on many of the compounds investigated (Abstr., 1896, ii, 511). L. M. J.

Specific Heats of Gaseous Elements and their Atomic Constitution. By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1897, **124**, 119—125).—The author summarises the known facts with respect to the specific heats of the gaseous elements. He points out that there are four distinct cases, (1) where the ratio of the two specific heats is 1·66, and the molecules are generally believed to be monatomic; (2) where the ratio is 1·41, and the molecules behave as if they were diatomic and show no signs of dissociation into monatomic molecules, although at high temperatures there are indications that such dissociation is beginning to take place; (3) where the ratio is 1·30

(chlorine, bromine, and iodine) and the diatomic molecules dissociate more or less completely at high temperatures. In these cases, the ratio indicates that a considerable amount of internal work is done when the temperature of the gas is raised between ordinary limits; (4) where the ratio is 1·175 and the molecule is tetratomic, but becomes diatomic at high temperatures. The specific heats at constant volume are in the four cases 3·0, 4·8, 6·6, and 11·4, and the ratios of the three chief numbers are not far removed from 1 : 2 : 4. There is, therefore, some ground for supposing that the specific heats of elementary gases at constant volume are proportional to the number of atoms in their molecules. C. H. B.

Variation of Melting Points with the Pressure. By R. DEMERLIAC (*Compt. rend.*, 1897, **124**, 75—77).—Between 1 atmosphere and 10 atmospheres, the variations in the melting points with variations in the pressure are, in the cases of paratoluidine and α-naphthylamine practically identical with those calculated by means of Clapeyron's formula. The author has also made experiments with a view of ascertaining whether this formula holds good at high pressures. In the case of benzene, observations were made between 10 and 450 atmospheres, and when the results are plotted with the rise in melting point for ordinates and the pressures for abscissæ, the curve is concave towards the axis of the pressures. The curve is a hyperbola, and beyond 330 atmospheres it becomes approximately parallel with the axis of the pressures, or, in other words, dT/dp tends towards zero. In the case of paratoluidine, the curve is also a hyperbola, and dT/dp tends towards 0 when p increases beyond 180 atmospheres. α-Naphthylamine gives a curve of the same kind, and dT/dp tends towards zero when p exceeds 150 atmospheres. C. H. B.

Thermochemical Method for the Determination of the Equivalents of Acids and Bases. By MARCELLIN P. E. BERTHELOT (*Ann. Chim. Phys.*, 1896, [vii], **7**, 283—288).—The author describes a thermochemical method by which the equivalent of an acid or a base may be determined, even if the composition of the compound is unknown. A given weight, p, of the acid is made up with distilled water to a given volume, say two litres; a known quantity of this solution, say 500 c.c., is then taken, 100 c.c. of potash of known strength (KOH = 2 litres) is added, and the heat evolved, q_1, is measured. A second 100 c.c. of the potash solution is added, and the heat evolved, q_2, is also measured, the operation being repeated until, on the addition of fresh alkali, no more heat is developed. The total heat of combination thus measured $(q_1 + q_2 + \ldots\ldots + q_n)$ is one-quarter of that which the given weight, p, of the acid would evolve. The equivalent, E, of the acid can then be obtained by the equation $E = \frac{2000}{400n} p = \frac{5p}{n}$, and is approximate to $1/n$th.

It is necessary that the amount of alkali added in the first instance should be insufficient to neutralise all the acid taken, otherwise p_2, p_3, &c., become 0. In order to determine the equivalent more accurately,

the experiments must be repeated, using the same strength of acid, but the potash only $\frac{1}{10}$th as strong; by this means the equivalent will be approximate to $\frac{1}{10}n$. The approximation can be made even closer by using more dilute solutions of potash.

In the case of monobasic acids, the numbers q_1, q_2, &c., are equal among themselves; in the case of many polybasic acids, however, these numbers differ considerably, decreasing, as a rule, with each fresh addition of alkali.

The same rules apply for the determination of the equivalent of a base, but in all cases the rules only apply to soluble acids or bases yielding soluble salts. Special precautions are necessary in the case of an insoluble acid, an insoluble base, or an insoluble salt resulting from a soluble acid and base. J. J. S.

Thermochemical Relations between the different Modifications of Ordinary Glucose. By MARCELLIN P. E. BERTHELOT (*Ann. Chim. Phys.*, 1896, [vii], **7**, 51—57. Compare Béchamp, Abstr., 1894, ii, 2; Tanret, Abstr., 1895, i, 490).—The author gives the following thermochemical data at 20°.

	D. Solution.	N. Heat evolved by the action of 5/2 NaOH on the Solutions.	D + N.
	Cal.	Cal.	Cal.
α-Glucose ($\alpha_D = 106°$)	−2·15	+3·75	+1·45
β-Glucose ($\alpha_D = 52·5°$)	−0·96	+3·96	+3·00
γ-Glucose ($\alpha_D = 22·5°$)	−1·42	+3·75	+2·33

It is therefore to be inferred that

(1) The change of α-glucose into β-glucose absorbs −1·55 Calories.
(2) The „ „ γ-glucose „ „ „ −0·67 „

The differences are even less for the compounds in solution, in fact they fall within the limits of experimental error. J. J. S.

Pressure Differences produced by Isothermal Distillation. By MAX REINGANUM (*Ann. Phys. Chem.*, 1896, [ii], **59**, 764—767).—Experiments of Askenasy are described in which a tube about 1 metre long was closed at one end (previously somewhat enlarged and funnel-shaped) with a plug of plaster of Paris, filled with water saturated with gypsum, and then placed in a vessel of mercury, the closed end uppermost. Evaporation of the water through the plaster plug took place, this being hastened as far as possible by keeping the surrounding atmosphere dry, and the mercury rose in the tube to heights (893 mm.!) which were greater than those of the barometer at the time. The author shows that, in cases of this kind, if p is the vapour pressure of water at the surface level of the mercury, p' the vapour pressure at the level of the plaster plug, so that $p - p'$ is the hydrostatic pressure of a column of water vapour of the height of the tube, the mercury should then rise to the height $H' = (p - p')/(p + p') \times s \times 691·6\ T$ cm., where s is the specific gravity of mercury, and T the absolute temperature at the time of the experiment. H. C.

Vapour Pressure of Compounds of Calcium Chloride with Water. By WILHELM MÜLLER-ERZBACH (*Zeit. physikal. Chem.*, 1896, 21, 545—555).—The vapour pressures were estimated by the method previously adopted (Abstr., 1896, ii, 295), and the following results were obtained.

Compound.	Temp.	Vap. Pres.	V.P. / V.P. of Water.
$CaCl_2 + 4—6H_2O$	15·5°	2·47	0·192
	16·7	2·83	0·20
	28·0	7·02	0·25
$CaCl_2 + 2—4H_2O$	15·0	1·47	0·116
	33·0	5·98	0·16
	13·6	1·57	0·135
$CaCl_2 + 1—2H_2O$	15·0	0·64	0·05

The results agree fairly well with Roozeboom's determinations, but the author does not find two modifications of the compound $CaCl_2 + 4H_2O$, which are stated by Roozeboom to exist. The capability of forming a plastic mass, possessed by some salts, such as calcium chloride, the author considers to be due partly to the absorption of moisture from the atmosphere, but more particularly to inherent plasticity of the salt. The redetermination of the vapour pressure of sulphuric acid gave results in accordance with those of Regnault, except in the case of a strong acid, the value 0·061 being obtained, in place of 0·074 for acid of sp. gr. 1·614 at 15°. L. M. J.

Internal Friction of Mercury Vapour. By ARTHUR A. NOYES and H. M. GOODWIN (*Zeit. physikal. Chem.*, 1896, 21, 671—679).—The internal friction of a gas is dependent on the mass and volume of the molecule, the mean velocity and the mean free path, and if the values for different gases are compared, the relation obtained is $\eta_1 : \eta_2 = m_1c_1/q_1 : m_2c_2/q_2$, where η is the coefficient of friction m the mass of the molecule, c the mean velocity, and q the cross section of the molecule or its sphere of action. At equal temperatures, however, $m_1c_1^2 = m_2c_2^2$, so that the relation reduces to $q_1 : q_2 = \eta_2/\eta_1 \cdot \sqrt{m_1/m_2}$, and comparisons of q may be made. Experiments were made with mercury, carbonic anhydride, and hydrogen, under similar conditions and with the same apparatus, and the results obtained were: $\eta Hg/\eta CO_2 = 2·17$; $\eta Hg/\eta CO_2 = 2·08$; $\eta Hg/\eta H_2 = 4·04$. From these results, the ratios $qHg/qCO_2 = 1·02$ and $qHg/qH_2 = 2·48$ are obtained, so that the cross section, and hence probably the volume, of the monatomic mercury molecule is practically identical with that of the complex carbonic anhydride molecule, a fact which appears to indicate that in molecules the interatomic spaces are very small. The density of the mercury molecule is about 4·5 times greater than that of carbonic anhydride. L. M. J.

Some Peculiarities of Solubility Curves. By HENRI L. LE CHATELIER (*Zeit. physikal. Chem.*, 1896, 21, 557—560.)—If curves be constructed with melting points as ordinates and equivalent composi-

tion of the melted portion as abscissæ, maxima usually occur in the neighbourhood of points where the composition is that of a definite compound, whilst in certain cases, for instance, a mixture of lithium and potassium carbonates, the maximum is reduced to a point. Curves of this nature are given for this mixture and for alloys of aluminium-copper, tin-copper, and antimony-copper. Theoretical investigations show that, in general, the composition of the melted part is different from that of the mixture, and that points occur as maxima when the compound formed is not dissociated in the solution. L. M. J.

Law of Contraction on Dissolving Sugar in Water. By ALFRED WOHL (*Ber.*, 1897, **30**, 455—460).—The contraction dv of a solution of x grams of cane-sugar in a volume of water V is best represented by the equation

$$\frac{dv}{V} = a \cdot \frac{x(l-x)}{V^2}$$

$$dv = a \cdot \frac{x(l-x)}{V}$$

$$a = \frac{dv \cdot V}{x(l-x)}$$

The most probable value of the constant a being 0·00303.

It is possible therefore with sufficient accuracy to determine the contraction by means of the formula

$$dv = 0{\cdot}00303 \frac{x(l-x)}{1-\sigma x}$$

whence

$$\sigma = 0{\cdot}36965 = 1 - \frac{1}{s}$$

and therefore the specific gravity of the solution

$$s = \frac{(1-\sigma x)}{(1-\sigma x)^2 - 0{\cdot}00303\, x(l-x)}.$$

J. F. T.

Rate of Reduction of Chromic Acid by Phosphorous Acid. By GEORGES VIARD (*Compt rend.*, 1897, **124**, 148—151).—The author has determined the rate of interaction of chromic acid and phosphorous acid in solutions of various degrees of concentration. The change can be approximately represented by the equation $dx/dt = K(A-x)^4$, where A is the initial quantity of chromic acid and x the quantity reduced in the time t. It follows that $t = \frac{1}{3}KA^3 \times A_3 - (A-x)^3/(A-x)^3$, and if $C = 3KA^3$, $(A-x)^3 = A^3/(1+Ct)$.

The value of C increases with the concentration of the solution; it also varies with the time in one and the same solution, and reaches a maximum when about half the chromic acid is reduced, afterwards diminishing regularly. In dilute solutions, the variations with the time are much less, and the observed and calculated values of x agree much more closely. Curves plotted with t as abscissæ and C as ordinates show the influence of dilution on the reaction, and if the curves are continued until they cut the axis of C, an initial value of C

is obtained, which differs from the initial velocity, KA^4, by a constant only. It can then be proved that the initial velocity varies according to a power of the concentration, the exponent being 1·4.

C. H. B.

Classification of Chemical Elements. By P. E. Lecoq de Boisbaudran (*Compt. rend.*, 1897, **124**, 127—130).—In the table previously given (Abstr., 1895, ii, 440), it is not necessary to place hydrogen at the bottom of each column. It may be placed below lithium only, but in the particular arrangement this would imply the existence of an unknown element below beryllium, and of negative elements below the other families. The latter are, in reality, represented by the three elements of high atomic weights, Bi, Pb, Tl. The changes in the atomic weights of Be, Li, $(?\beta)''$ and $(?\alpha)'$ show that if the elements were *below* N, C, and B, they would have negative atomic weights, which is inadmissible.

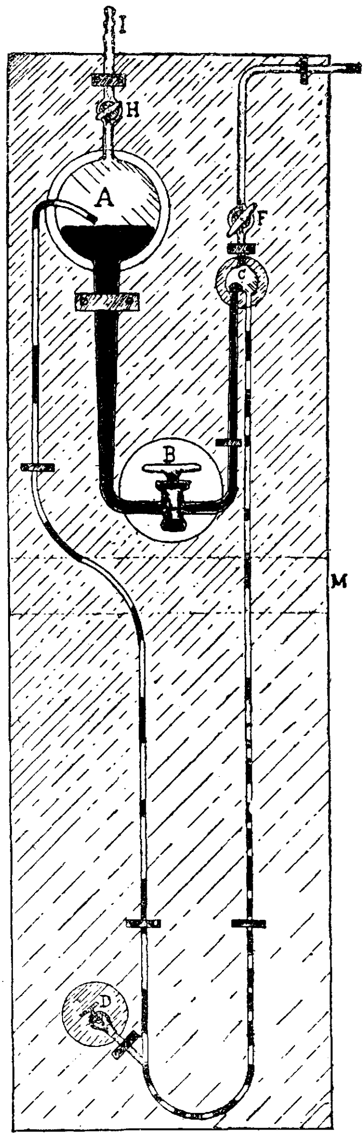
The author denotes by the term "bascule," the difference between the atomic weights of a pair of odd and even elements and their mean atomic weight, and he shows, amongst other things, that these bascules are at a minimum at the nodes (*loc. cit.*) This would not be the case if Mg – Na were placed on the same level as Si – Al and S – P.

The bascule, Te – Sb, is greater than that of Sn – In, and the bascule $(?\zeta)''$ – I, seems to be greater than that of Ba – Cs. It follows that iodine occurs at the base of a high bascule and tellurium at the summit of another high bascule, and consequently the atomic weight of tellurium may be higher than that of iodine, although the mean of Te + Sb (124·25) may be lower than the mean of $(?\zeta)$ + I (129·95). The rule as to the progressive increase in atomic weights must be applied to the means of pairs of odd and even elements, and not to isolated elements. C. H. B.

Methods of Determining the Molecular Weights of Homogeneous Liquids. By Isidor Traube (*Ber.*, 1897, **30**, 265—277).—The author gives a summary of all the methods at present available for the purpose of determining the molecular complexity of liquids (compare Ramsay, Abstr., 1895, ii, 40, and Linebarger, Abstr., 1896, ii, 9). In former papers, it has been shown that the molecular co-volume for non-associated liquids is 25·9 at 15°. For the double molecule, the co-volume is 12·95, and, generally, if the co-volume has any value y, between 12·95 and 25·9, the association factor will be given by $x = 1 + \frac{25 \cdot 9 - y}{12 \cdot 95}$. This is the simplest of all methods for determining the value of the factor of association, as it is thus found from a single determination of the specific gravity. The author gives tables of the values of x thus found and of the values obtained by other methods, showing the general agreement in the different cases.

H. C.

A Simple Automatic Sprengel Pump. By B. B. Boltwood (*Amer. Chem. J.*, 1897, **19**, 76—78).—In this pump (see the accompanying cut), the funnel of the ordinary Sprengel is replaced by a globe, A, provided with a tap, H, and a tube, I, which is connected with



a good water pump. The mercury, after passing C, falls down the vertical tube, and is swept up the left-hand branch by air, which is admitted at D, and in this way is returned to the globe, A, the action being thus rendered continuous.

A. H.

Inorganic Chemistry.

Conversion of Hypochlorites into Chlorates. By IYOTIBHUSHAN BHADURI (*Zeit. anorg. Chem.*, 1897, 13, 385—406).—When solutions of sodium hydroxide, of concentrations varying from 1·5 to 25 per cent., are treated with chlorine at 25—33°, very little chlorate is formed. The conversion of hypochlorite into chlorate is evident in solutions of 10 per cent., and in solutions above 20 per cent. the duration of the experiment has a great influence on the decomposition. Strongly alkaline solutions of sodium hypochlorite, if allowed to remain in the dark at 25—28° for some time, slowly decompose, yielding chlorate, sodium chloride, and oxygen; the decomposition is more pronounced when the solution is exposed to red light, and still more so when exposed to yellow light.

A solution of sodium hydroxide (5 per cent.) was saturated with chlorine, the excess of chlorine removed by a current of dry air free from carbonic anhydride, and an alkaline solution of sodium hypochlorite then gradually added until free chlorine was no longer present. This solution was very unstable, and in the course of an hour its titration factor altered greatly. After remaining in a closed flask in the dark for 3 hours, it was found that free chlorine was evolved, but on shaking the flask, this was again absorbed. It therefore appears that, under some conditions, sodium hypochlorite decomposes into chlorine and alkali.

When a solution of sodium hypochlorite is kept under diminished pressure, a regular evolution of oxygen takes place.

When solutions of sodium hypochlorite of various strengths are heated at 100° in sealed tubes in the dark for various periods of time, the percentage decomposition, in solutions in which the relative quantities of alkali, chloride, chlorate, and hypochlorite are the same, decreases with the dilution until a minimum is reached, and then, on further dilution, again increases; this point is reached when 1·6 per cent. of sodium hypochlorite is present. An aqueous solution of sodium hypochlorite is most stable, therefore, when the number of salt molecules in the solution is about 0·4 per cent. The amount of oxygen evolved after one hour is about $\frac{1}{4}$ to $\frac{1}{2}$ the amount in the chlorate which is formed. On further heating, the amount of free oxygen increases, but is never more than that contained in the chlorate. The relative amount of free oxygen increases with the dilution of the solution, and decreases with the rapidity with which the solution is heated. E. C. R.

Hypoiodous Acid and Hypoiodites. By ROBERT L. TAYLOR (*Chem. News*, 1897, **75**, 97).—The author confirms and extends Schönbein's observation. Aqueous solutions of iodine yield, in the presence of an alkali, a solution of potassium iodide and hypoiodite; whilst with silver salts and mercuric oxide, hypoiodous acid is formed; stronger solutions can be obtained by the use of iodine water with iodine in suspension. The solution from the alkali bleaches indigo strongly, but not litmus, that from the silver salts bleaches to a less extent, and that from the mercury only very feebly; but the latter can be rendered strongly bleaching by adding a small quantity of alkali. All the solutions are completely decomposed by boiling. D. A. L.

Absorption of Hydrogen Sulphide by Melted Sulphur. By H. PÉLABON (*Compt. rend.*, 1897, **124**, 35—37).—When sulphur and hydrogen are heated together in sealed tubes at 440°, hydrogen sulphide is formed and is absorbed by the molten sulphur, but is liberated as the latter solidifies, the phenomena being analogous to the "spitting" of silver. Hydrogen is not absorbed by liquid sulphur.

When hydrogen sulphide and sulphur are heated together, there is distinct absorption at 170°, but the quantity absorbed is much less than at 440°, and, in fact, between these limits it is higher the higher the temperature. Even boiling sulphur at ordinary pressure absorbs considerable quantities of the gas. The phenomena are very different from those of ordinary solution; at 440°, in a vacuum, the sulphur retains the whole of the absorbed gas, and only liberates it during solidification.

Hydrogen and sulphur begin to combine at 250°, but between this point and 350° combination is not complete. C. H. B.

Density of Ozone. By MARIUS OTTO (*Compt. rend.*, 1897, **124**, 78—81).—A glass flask was filled with oxygen and weighed, and afterwards filled with ozonised oxygen and again weighed. The ozone was next estimated by absorbing it in potassium iodide solution acidified with sulphuric acid. The result of two concordant experiments is that the density of ozone is half as high again as that of oxygen, or 1·6584. C. H. B.

Action of Ammonia on Tellurium Tetrachloride: Tellurium Nitride. By RENÉ METZNER (*Compt. rend.*, 1897, **124**, 32—35).—Tellurium tetrachloride is completely reduced by dry ammonia at 200—250°, with formation of ammonium chloride and liberation of nitrogen. At 0°, the chloride combines with the ammonia to form a yellowish compound, $TeCl_4,3NH_3$, which loses ammonia at the ordinary temperature, is decomposed by water with formation of tellurous acid, and by aqueous potash with evolution of ammonia. When heated, it blackens, gives off ammonia, and then a dark mixture of ammonium chloride and tellurous chloride volatilises.

If carefully dried ammonia is allowed to act on the chloride in a specially constructed apparatus, and the product is treated with liquid ammonia, washed repeatedly with this liquid, and finally with water, tellurium nitride, TeN, is obtained as an amorphous, friable, lemon-yellow compound. It detonates with great violence under percussion, or when heated to about 200°. It is not, however, decomposed by water nor by dilute acetic acid, but aqueous potash liberates all the nitrogen in the form of ammonia. C. H. B.

Action of Hydrogen Sulphide and Hydrogen Selenide on Phosphorus Oxychloride. By J. ADOLPHE BESSON (*Compt. rend.*, 1897, **124**, 151—153).—When hydrogen sulphide is dissolved in phosphorus oxychloride at 0°, and the solution is allowed to remain in a closed vessel, a yellowish-white, amorphous precipitate forms in about 24 hours, and after many weeks small, acicular crystals also separate. The amorphous product and the crystals have the composition $P_2O_2S_3$, and the former can be crystallised by dissolving it in phosphorus oxychloride in a closed vessel at 150°. When heated at 150°, the oxysulphide yields a sublimate of pentasulphide, and if heated in a vacuum at 200° for several hours, it completely decomposes into pentoxide and pentasulphide. It is slowly decomposed by water and moist air with liberation of hydrogen sulphide, burns in air or oxygen, and is violently oxidised by nitric acid.

If the solution of hydrogen sulphide in phosphorus oxychloride is heated at 100°, or, better, if the oxychloride is heated in a closed vessel with an open tube containing hydrogen persulphide, all the hydrogen sulphide is replaced by hydrogen chloride and the thio-oxychloride, $P_2O_2SCl_4$, is formed. It is a colourless liquid with a peculiar odour, and is slowly decomposed by water; it boils at 104° under a pressure of 10 mm. and at 119° under a pressure of 30 mm., and does not solidify at −30°. When heated in a vacuum at 300—350°, it yields a sublimate of phosphorus pentasulphide followed by one of the pentoxide, whilst a vitreous residue is left containing phosphorus, sulphur, and chlorine.

Hydrogen selenide has no action on the oxychloride at the ordinary temperature, but acts slowly at 100°, the products being brown phosphorus pentaselenide and metaphosphoryl chloride, PO_2Cl. The reaction is represented by the equation, $4POCl_3 + 5H_2Se = 10HCl + P_2Se_5 + 2PO_2Cl$. C. H. B.

Action of Chlorine and Steam on Red-hot Carbon. By ALEXANDER NAUMANN and F. G. MUDFORD (*Ber.*, 1897, **30**, 347—354)

—The primary reaction is represented by the equation $2Cl_2 + 2H_2O + C = 4HCl + CO_2$, and not, as Lorenz states (Abstr., 1896, ii, 17), by $Cl_2 + H_2O + C = 2HCl + CO$. Some carbonic oxide is undoubtedly formed, but this is due to a secondary action of carbon on the carbonic anhydride first formed, as is proved by the fact that the amount of carbonic oxide is increased when the layer of carbon is made longer, or the gases are passed more slowly through the heated tube. In the presence of excess of chlorine, a certain amount of carbonic oxide is oxidised to anhydride: $Cl_2 + H_2O + CO = 2HCl + CO_2$.

In the presence of excess of steam, no chlorine passes over unchanged, but some hydrogen is formed, and more of it in proportion as the temperature is higher, and the contact of the gases with the carbon of longer duration.

Lastly, it is pointed out that all these processes, resulting in the formation of hydrogen chloride, are exothermic, and that in consequence, when once the action is started, no further supply of external heat should be necessary; this is important from the point of view of a possible technical application of the processes. C. F. B.

Helium. By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1897, **124**, 113—119).—The author has repeated his experiments on the action of a silent discharge on argon in presence of benzene, and confirms his earlier statements (Abstr., 1895, i, 412).

When helium is treated in the same way, there is not at first any luminous phenomenon visible by daylight, but after 11 or 12 hours' action of the discharge a characteristic orange luminescence appears and gradually increases in intensity. Its spectrum under atmospheric pressure shows the lines 587·5, 516·0 and 500·0 of helium, the line 546 of mercury, and the hydrocarbon band at about 426. After 17 hours' action of the discharge, with successive additions of small quantities of benzene, 13·7 per cent. of helium was absorbed, and this was increased to 16 per cent. in 39 hours. The product is a resinous solid similar to that obtained with argon.

Under similar conditions, but in presence of carbon bisulphide in place of benzene, helium is absorbed in the same way as argon. There is, however, no continuous luminescence, but only a "rain of fire" at the surface of contact of the gas and the mercury; some of the helium lines are shown, however. After 182 hours' action 55·5 per cent. of the helium was absorbed, and this was raised to 68·4 per cent. after 210 hours.

When the product is heated in a vacuum, helium is liberated, and after removal of carbon bisulphide and a trace of carbonic oxide (resulting from action on the glass), it again behaves in exactly the same way when subjected to the action of the discharge in presence of benzene.

The gas not absorbed in the first experiments even after prolonged action of the discharge, if brought in contact with fresh benzene and mercury and again subjected to the discharge, shows the characteristic luminescence, and is gradually absorbed.

Helium, like argon, is not affected by the action of the discharge in presence of mercury only. C. H. B.

Artificial Colouring of Crystals of the Haloid Salts of the Alkali Metals by means of Sodium and Potassium Vapour. By FELIX KREUTZ (*Ber.*, 1897, **30**, 403. Compare Giesel, this vol., ii, 170). —A claim to priority. (See Kreutz, *Anz. Akad. Wiss.*, *Krakau*, April, 1892). M. O. F.

Alkali Trihaloids. By CHARLES H. HERTY and HOMER V. BLACK (*Amer. Chem. J.*, 1896, **18**, 847—849. Compare Abstr., 1896, ii, 474).—An investigation to determine whether the mixed trihaloids of the alkali metals are isomorphous mixtures or true chemical compounds. The results obtained with rubidium dibromiodide confirm the latter supposition, the successive crops of crystals obtained from a solution of the ingredients in the requisite proportions being identical in composition. A. W. C.

Action of Halogen Hydracids on Solutions of the corresponding Alkali Salts. By ALFRED DITTE (*Compt. rend.*, 1896, **123**, 1281—1283).—When hydrofluoric acid is added to a saturated solution of potassium fluoride, the solubility of the latter rapidly diminishes from 963 grams per 1000 grams of water to 324·6 grams per 1000 when 40·3 grams of hydrogen fluoride are present. From this point the solubility decreases very slowly with addition of more acid, reaches a minimum of 295·7 grams in 1000 when 113·6 grams of acid are present, and then increases somewhat rapidly as the proportion of acid increases. With sodium fluoride, the phenomena are similar, and the two curves have the same general character, although the actual quantity of salt dissolved is very much less. The minimum of 22·5 grams in 1000 is reached when 45·8 grams of acid is present. Analogous phenomena are observed with bromides and iodides, and they will be described in detail in a subsequent memoir. The numbers agree with Berthelot's calorimetric determinations which indicate the existence of more or less completely dissociated compounds of the salt and hydracid.

C. H. B.

Action of Alkali Hydroxides on Solutions of the corresponding Halogen Salts. By ALFRED DITTE (*Compt. rend.*, 1897, **124**, 29—32).—When potassium hydroxide is added to a solution of potassium bromide, the solubility of the latter decreases as the proportion of the former increases. At first the curve is practically rectilinear, but afterwards the weight of bromide precipitated by a given weight of hydroxide diminishes as the total quantity of hydroxide present increases.

With sodium bromide, which can form a hydrate, the phenomena are different. The solubility of the bromide at first diminishes rapidly as the proportion of hydroxide increases, and then the rate of diminution becomes much slower, and between certain limits the total quantity of solid matter in solution remains constant. Finally, precipitation of the bromide again begins, and the solubility diminishes rapidly as the proportion of hydroxide increases. The curve seems to be formed of two distinct branches, one of which corresponds with a hydrated and the other with the anhydrous bromide.

Potassium chloride and iodide and sodium chloride, which do not form

hydrates, behave like potassium bromide. Sodium iodide and potassium fluoride, which do form hydrates, behave like sodium bromide, and give a curve with two parts. The intermediate section of the curve probably represents a condition of complex equilibrium in liquids containing both the hydrated and anhydrous salts. Even in solutions containing a large proportion of hydroxide, the curves give no indication of the formation of a compound of the hydroxide and the salt. C. H. B.

Action of Hydrogen Chloride on Alkali Sulphates. By ALBERT COLSON (*Compt. rend.*, 1896, **123**, 1285—1288).—Contrary to the general belief, sodium sulphate dried at 150° is attacked by dry hydrogen chloride at the ordinary temperature. When a large quantity of the sulphate is in contact with a small quantity of the gas, which corresponds with the maximum development of heat, the pressure of the gas after equilibrium has been established is independent of its mass. With 10 grams of the salt and 93 c.c., and 180 c.c., of gas, the pressures observed were

t	10°	100°	120°	175°	120°
p.	2	15	23	77	24 mm.

If the temperature is suddenly raised, the pressure developed is at first considerably higher than that properly corresponding with the temperature, but gradually returns to its normal value. This result is most probably due to the co-existence of several phases of the reaction and the superposition of one phase on another. The co-existence of several phases is due to the slowness with which equilibrium is reached and differentiates dissociation in multiple phases from dissociation in successive periods such as that observed by Isambert with ammoniosilver chloride.

With excess of sodium chloride in place of sodium sulphate (2·8 grams of sodium chloride and 1·8 grams of sulphuric acid), the pressures were also independent of the mass of hydrogen chloride present, and were as follows:

t	0°	8·2°	37°	100°
p.	128	135	163	262—320 mm.

With the system $NaHSO_4 + HCl = H_2SO_4 + NaCl$, the maximum pressure at 0° exceeds 2650 mm. In addition to this system, the phases in which the author imagines the reactions to take place and which correspond respectively to the pressures given above are, $Na_2SO_4 + 2HCl = H_2SO_4 + 2NaCl$ and $2Na_2SO_4 + 2HCl = 2HNaSO_4 + 2NaCl$. A fourth phase may result from the combination of sulphuric acid with the sodium hydrogen sulphate. C. H. B.

Decomposition of Metallic Sulphates by Hydrochloric Acid. By ALBERT COLSON (*Compt. rend.*, 1897, **124**, 81—84).—When excess of dry lead sulphate is brought in contact with dry hydrogen chloride, the pressure of the hydrogen chloride depends on the temperature, and is independent of the mass of the gas present. If the solid is afterwards treated with alcohol, sulphuric acid is dissolved, and hence it would seem that this acid is partially displaced by hydrogen chloride. It is possible, however, that the alcohol disturbs the conditions of equilibrium.

When dry hydrogen chloride comes in contact with dry cupric sul-

phate, the latter changes from white to yellow-brown. The pressure of the gas depends on the temperature, and not on the mass of gas present.

If lead sulphate is placed in a vessel of porous earthenware and treated with hydrogen chloride at 0°, and the salt is afterwards completely removed, it is found that the earthenware has absorbed a considerable quantity of sulphuric acid, which must therefore have been liberated. Similar results are obtained if the lead sulphate, after treatment with the gas, is squeezed between asbestos paper; the latter absorbs a considerable quantity of free sulphuric acid.

On the other hand, sulphuric acid does not decompose lead chloride at 15° in an atmosphere of hydrogen chloride. The tension of dissociation at 15° is less than half an atmosphere, and decomposition does not take place until the pressure is reduced.

The displacement of a volatile by a non-volatile acid of the same energy is not determined solely by the volatility of the displaceable acid, and, as a rule, heat or alteration of pressure is necessary in order to produce a change. The displacements is analogous to heterogeneous dissociations, and the maximum pressure at the ordinary temperature is usually less than one atmosphere.

In reversible chemical phenomena, as for saturated vapours, the heat developed, L, is connected with the absolute temperature, T, and the pressure, p, by the relation $L = T/425\ (u' - u)\ dp/dT$, u' being the volume of 1 kilogram of the substance when completely volatilised, and u the volume of the same mass condensed. C. H. B.

Action of Lithium on Carbon and certain Carbon Compounds. By ANTOINE GUNTZ (*Compt. rend.*, 1896, **123**, 1273—1275).—Lithium carbide, C_2Li_2, is formed when lithium is heated to redness in a vacuum with carbon, or when it is heated in a current of carbonic oxide or carbonic anhydride. In the latter case, the current of gas must be slow, so that the temperature does not rise above a dull red heat; at a bright red heat, very little carbide is formed. When the metal is heated in ethylene or acetylene, a mixture of carbide and hydride is formed, but methane has practically no action. If the nitride, instead of the metal, is heated with carbon, the carbide is mixed with a large proportion of cyanide, and the cyanide is also formed in considerable quantity when the metal is heated in a carbon dish in a current of nitrogen for the preparation of the nitride. C. H. B.

Silver Hydride. By EDWIN J. BARTLETT and WILLIAM F. RICE (*Amer. Chem. J.*, 1897, **19**, 49—52).—When hypophosphorous acid is added to silver nitrate solution, the mixture becomes wine-red, then black, and finally deposits a black, flocculent precipitate. If the precipitate is left in the solution, it is converted into metallic silver, but, on the other hand, if it is collected, washed, and dried at 60°, it consists of *silver hydride*; it loses 0·7 per cent. when ignited, metallic silver being left. The authors do not experimentally prove that the loss on ignition is due to hydrogen. A. H.

Calcium Carbide; a new Reducing Agent. By HENRY N. WARREN (*Chem. News*, 1897, **75**, 2—3).—The oxides of lead, copper, tin, iron, manganese, nickel, cobalt, chromium, molybdenum, and tung-

sten yield calcium alloys when heated with calcium carbide. The alloy in the case of lead is brittle and sonorous when struck, it melts at a lower temperature than pure lead, and acts less energetically towards water than lead alloys with the alkali metals. The presence of the calcium renders copper cold-short, and iron brittle and very oxidisable in contact with water. D. A. L.

Action of Boron on Iron and Steel, and Errors in Iron Analysis caused by the Presence of Boron. By HENRY N. WARREN (*Chem. News*, 1897, **75**, 91).—"Boron-eisen" can be obtained by melting ferric borate under a layer of borax; the compound obtained scratches flint; moreover, iron becomes contaminated with boron merely by heating the cast metal with fusible borates, or by reducing its oxide by means of carbon in the presence of a fusible borate; the amount of boron thus entering into combination amounting to from $\frac{1}{2}$ to 2 per cent. D. A. L.

Action of Dissolved Carbonic Anhydride on Iron. By PAUL PETIT (*Compt. rend.*, 1896, **123**, 1278—1280).—When water containing 638 milligrams of calcium carbonate per litre dissolved in carbonic anhydride, but neutral to phenolphthalein, is brought in contact with finely powdered iron, more than half the carbonate is precipitated, and iron is dissolved. Water saturated with carbonic anhydride will dissolve as much as 500 milligrams of iron per litre, with liberation of an equivalent quantity of hydrogen. The iron is converted into ferrous carbonate, and if the solution is exposed to air, ferric oxide is precipitated.

The water of the Moselle was found to dissolve 3·15 milligrams of iron per litre; if previously treated with a current of carbonic anhydride for a few minutes, it dissolved 200·6 milligrams; but if mixed with lime-water until slightly alkaline to phenolphthalein, it dissolved no iron at all.

Water containing about 0·1 gram per litre of calcium chloride, sodium chloride, potassium sulphate, or calcium nitrate, but no carbonic anhydride, dissolved only minute traces of iron, although a notable amount of iron was oxidised, sodium chloride being most active, and potassium sulphate coming next. If the solutions are saturated with carbonic anhydride, the quantity of iron oxidised but not dissolved remains practically the same, but the quantity of iron dissolved in each case is considerable, and is decidedly largest with potassium sulphate, the same with the sodium chloride solution as with water, less with calcium chloride, and considerably less with calcium nitrate. The potassium sulphate solution becomes alkaline, and the residue contains iron sulphide. With this exception, the action peculiar to each salt is independent of the presence of carbonic anhydride.

When air has access to the solutions, the quantity of iron dissolved remains practically the same, but the quantity of iron oxidised increases enormously. C. H. B.

Action of Water of the Hubb Coal Mine on Cast Iron. By FRANK W. DURKEE (*Amer. Chem. J.*, 1896, **18**, 849—858).—Cast iron for some time submerged in the water of the mine was found to have become changed to a mass resembling graphite, and soft enough to be

easily cut with a knife. Analyses of the original and of the transformed cast iron showed that the latter had lost considerably in percentage of iron and gained in oxygen.

The presence of ferrous sulphate in the water of the mine is accounted for by supposing that the iron pyrites in the coal has been acted on by moist air, and the sulphuric acid thus formed has attacked the cast iron, thus accounting for the loss of iron.

The oxide of iron found in the transformed cast iron is supposed to be due to a secondary chemical action, whereby the oxygen of the air dissolved in the water had attacked the original cast iron.

A. W. C.

Pure Carbide of Iron. By EDWARD D. CAMPBELL (*Amer. Chem. J.*, 1896, **18**, 836—847).—Carbide of iron prepared by a method differing but slightly from that used by Arnold and Read (Trans., 1894, 788) was found on analysis to have the formula CFe_3; this carbide is soluble in hot, moderately concentrated hydrochloric acid, the gaseous products being hydrogen, butane, and probably ethane, butylene, and dibutylene. The probability of the existence of a series of ferrocarbons, with a general formula C_nFe_{3n}, analogous to the olefine series of hydrocarbons, is also discussed. A. W. C.

Volatility of Ferric Chloride. By HENRY P. TALBOT (*Amer. Chem. J.*, 1897, **19**, 52—59).—When a solution of ferric chloride is evaporated to dryness and the residue heated at 130° for 2 hours, no perceptible volatilisation of the salt occurs. If, however, an ammonium salt is present, or if the iron salt is evaporated with aqua regia, a slight loss does occur. A. H.

Silicide of Chromium. By GUILLAME J. L. DE CHALMOT (*Amer. Chem. J.*, 1897, **19**, 69—70).—When chromium sesquioxide, charcoal, and excess of silica are heated in the electric furnace, a crystalline *chromium silicide*, Si_2Cr, is produced. It occurs in long, grey needles, and is attacked by hydrofluoric acid. The product cannot easily be obtained free from silicon. A. H.

Reduction of Wolframite by Carbon in the Electric Furnace. By ED. DEFACQZ (*Compt. rend.*, 1896, **123**, 1288—1290).—Wolframite was mixed with 14 parts of sugar charcoal for 100 parts of the mineral and heated in an electric furnace for 12 minutes with an arc of from 950—1000 ampères and 50 to 60 volts. The metallic product contained 92·59 per cent. of tungsten and 5·08 per cent. of carbon, with some iron and silica. The slag consisted chiefly of calcium oxide with 10·75 per cent. of tungstic anhydride and some ferric oxide and silica. Neither the metal nor the slag contained manganese, although the original wolframite contained 15·9 per cent. of this element. C. H. B.

Recovery of Uranium from Residues. By A. GAWALOWSKI (*Zeit. anal. Chem.*, 1896, **35**, 678).—The author has improved his method (Abstr., 1877, i, 345) by replacing the ammonium carbonate by sodium carbonate (commercial ammonia soda), which is both cheaper and more efficient as a solvent for uranium phosphate. The bulk of the phosphoric acid is removed from the solution by adding ferric

chloride, and the remainder by adding magnesia mixture as long as it produces turbidity. The filtrate from the magnesia precipitate may either be acidified at once with acetic acid, or the uranium can be precipitated by adding hydrochloric acid, boiling off carbonic anhydride, and then adding excess of ammonia. M. J. S.

Alums of Vanadium Trioxide. By AUGUSTO PICCINI (*Zeit. anorg. Chem.*, 1897, **13**, 441—446; also Abstr., 1896, ii, 304).—*Potassium vanadium alum*, $K_2V_2(SO_4)_4 + 24H_2O$, is obtained in a similar manner to the alums previously described. It crystallises in transparent, greenish-violet crystals belonging to the cubic system. It is very easily soluble in water, crystallises only from the syrupy solution when cooled to 0—10°, and melts in its water of crystallisation at 20°, forming a green liquid; at the ordinary temperature, over sulphuric acid, it gradually loses part of its water; at 100°, it loses 35 per cent.; and becomes anhydrous at 230°. Sp. gr. = 1·782 at 4°/20°.

Thallium vanadium alum, $Tl_2V_2(SO_4)_4 + 24H_2O$, crystallises in pentagonal hemihedric or dyakisdodecahedric, reddish-violet crystals belonging to the cubic system. It is very easily soluble in warm water, somewhat less so in the cold. The crystals gradually alter when exposed to the air, and behave like the preceding salt when heated, becoming anhydrous at 230°, and leaving a yellowish-green residue. Sp. gr. = 2·342 at 4°/20°.

Sodium vanadium alum, $Na_2V_2(SO_4)_4 + 24H_2O$, crystallises from its syrupy solution at 0° in octahedra, and melts in its water of crystallisation at 9°.

The author gives a table of the specific gravities and solubilities of the vanadium alums and the refractive indices of the crystals.

E. C. R.

An Experiment with Gold. By M. CAREY LEA (*Zeit. anorg. Chem*, 1897, **13**, 447—448; also *Am. J. Sci.*, [iv], **3**, 64).—A beautiful green solution is obtained when a 10 per cent. solution of sodium hypophosphite is mixed with 1 c.c. of a gold chloride solution (10 c.c. = 1 gram of gold) and a drop of sulphuric acid; as soon as the solution begins to darken, 30 c.c. of water is added. This solution becomes gradually turbid, and a bluish-black precipitate of metallic gold is deposited. After filtration, the green filtrate again becomes gradually turbid, and this phenomenon can be observed many times. The green coloration is due to the presence of finely divided metallic gold precipitated in the blue modification; and if the solution is shaken and allowed to remain, a precipitate of gold is obtained on the sides of the containing vessel which is yellowish-brown by reflected light and bright blue by transmitted light. E. C. R.

Action of Phosphorus on Platinum. By A. GRANGER (*Compt. rend.*, 1896, **123**, 1284—1285).—When platinum is heated in phosphorus vapour in a current of carbonic anhydride at a temperature sufficient to start and maintain the action, the product is a greyish-black, lustrous, friable mass of the phosphide Pt_3P_5 described by Clarke and Joslin (Abstr., 1884, 400). Contrary, however, to the statement of these observers, the author finds that this phosphide is

completely soluble in aqua regia if the action is sufficiently prolonged. At high temperatures, a product is obtained which approximates in composition to PtP, and at a bright red heat the product retains only 4 per cent. of phosphorus.

When spongy platinum is used, the action takes place below a red heat, and the product is then the diphosphide PtP_2. Contrary to Schrötter's statement, the author finds that this compound is not completely soluble in aqua regia, and the part that dissolves has exactly the composition Pt_3P_5. C. H. B.

Mineralogical Chemistry.

Igneous Rocks from Smyrna and Pergamon. By HENRY S. WASHINGTON (*Amer. J. Sci.*, 1897, [iv], 3, 41—50).—Several andesitic rocks from near Smyrna and Pergamon, in western Asia Minor, are described; analyses are given of the following. I, augite-andesite from Mount Pagos, south of Smyrna; the fresh rock is dark grey, with numerous phenocrysts of labradorite, augite, and fewer of biotite, in a hyalopilitic ground-mass consisting of microlites of labradorite and orthoclase and a colourless glass; sp. gr. 2·640. II, augite-andesite from Kara Tash, west of Smyrna; this is a very dark, compact rock with numerous small labradorite, and few augite and biotite, phenocrysts in an almost black, highly vitreous ground-mass; sp. gr. 2·601. III, biotite-dacite from Pergamon; when fresh, this a dark grey rock with numerous phenocrysts of labradorite, biotite, hornblende, and some of sanidine, in a fine-grained or vitreous ground-mass; sp. gr. 2·525; here, although no quartz is present, the silica is high enough for the rock to be called a dacite.

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MgO.	CaO.	Na_2O.	K_2O.	H_2O.	Total.
I.	60·68	16·19	5·37	1·58	2·96	5·88	3·11	3·95	0·98	100·70
II.	61·93	18·47	1·93	2·23	2·66	4·31	2·92	3·92	2·28	100·65
III.	63·17	17·15	2·84	1·31	2·17	4·17	3·08	4·19	2·51	100·59

The rocks are compared with other volcanic rocks from western Asia Minor. L. J. S.

Missourite, a new Leucite Rock from Montana. By WALTER H. WEED and LOUIS V. PIRSSON (*Amer. J. Sci.*, 1896, [iv], 2, 315—323). —The Highland Mountain consists of an extinct group of greatly eroded volcanoes rising out of the plains of central Montana. The granular rock here described forms the irregular core or stock, 2½ miles long, of one of these denuded volcanic centres; it is situated at the head of Shonkin Creek, on the north side of the mountains. The freshest and coarsest-grained rock is dark grey, with a mottled appearance, much resembling a coarse-grained gabbro; it has the following percentage mineralogical composition:

Iron ore.	Augite.	Olivine.	Biotite.	Leucite.	Analcite.	Zeolites.
5	50	15	6	16	4	4

The structure is granular, but is wholly allotriomorphic; iron ore, apatite, and olivine have been first formed, whilst the leucite and augite have crystallised contemporaneously.

Leucite, separated from the powdered rock by means of a heavy liquid, gave analysis I, this agrees with the usual formula $KAl(SiO_3)_2$; average sp. gr. 2·44.

Analcite and a new zeolite have been formed by the alteration of the leucite. The small portion of the powdered rock which floated in liquid of sp. gr. 2·30 gave analysis II; it consists of a minute intergrowth of two minerals, one isotropic and probably analcite, the other with weak double refraction which, as shown by the analysis, is probably a potassium zeolite of the natrolite type. Deducting from II the constituents of analcite, the figures under III are obtained; these agree approximately with the formula $(K_2,Ca)Al_2Si_3O_{10} + 2H_2O$, which is like that of natrolite, but with potassium and calcium in place of sodium; a potassium zeolite would be the expected result of the alteration of leucite.

	SiO_2.	Al_2O_3.	Fe_2O_3.	MgO.	CaO.	K_2O.	Na_2O.	H_2O.	Total.
I.	54·46	22·24	0·68	trace	0·10	18·86	0·70	2·29	99·33
II.	50·18	25·07	trace	—	1·70	8·36	6·53	9·02	100·86
III.	45·85	26·07	—	—	3·12	15·35	—	9·61	100·00
IV.	46·06	10·01	3·17	14·74	10·55	5·14	1·31	1·44	

	FeO.	TiO_2.	P_2O_5.	MnO.	BaO.	SrO.	SO_3.	Cl.	Total (less O for Cl).
IV. cont.	5·61	0·73	0·21	trace	0·32	0·20	0·05	0·03	99·56

The bulk analysis of the rock by E. B. Hurlburt is given under IV; this is compared with analyses of a leucite-basalt, absarokite of Iddings, and shonkinite (Abstr., 1896, ii, 192). Here there is about the same silica percentage as in shonkinite, but there is more potassium, so that leucite has been formed instead of orthoclase. Leucite has not before been described as a constituent of a granular, plutonic rock.

L. J. S.

Composition of Hawaiian Soils and Rocks. By ALBERT B. LYONS (*Amer. J. Sci.*, 1896, [iv], 2, 421—429).—Several analyses are given of fresh and weathered volcanic rocks, and of the soils derived from these. I is the mean of 9 analyses of fresh lavas (the silica extremes are 35·86 and 58·06). II the mean of 3 analyses of tufa; this consists essentially of fragments of lava, more or less weathered, with also some fragments of coral limestone, &c. III is the mean of 3 analyses of "rotten" (weathered) lava. IV the mean of 10 analyses of soils; here the material was boiled for 2 hours in hydrochloric acid of sp. gr. 1·15, and the percentages are calculated from the weight of the ignited material. By this method, the insoluble residue consists almost wholly of silica and titanic anhydride, but contains some insoluble alkali silicates. I a, &c., are the same analyses calculated on the assumption that the Al_2O_3, and all the iron, as Fe_2O_3, have remained constant; this shows that there has been a considerable loss of silica, as well as of the more soluble constituents.

	I.	II.	III.	IV.	Ia.	IIa.	IIIa.	IVa.
SiO_2	47·86	41·79	21·32	40·00	1680	1393	320	800
TiO_2	3·63	—	7·33		128	—	110	
Al_2O_3	15·05	14·02	32·81	22·59	1000	1000	1000	1000
Fe_2O_3	8·59	14·69	33·92	30·05				
FeO	4·46	1·11	2·31		156	37	35	not est.
MnO	0·50	0·29	0·30	0·21	18	10	5	4
CaO	8·62	10·55	trace	1·26	303	352	—	22
MgO	6·08	10·73	0·58	1·19	213	358	9	20
Na_2O	4·22	1·99	0·47	0·50	148	66	7	9
K_2O	1·07	0·91	trace	0·43	37	30	—	8
CuO	0·19	0·09	0·30	—	7	3	5	not est.
P_2O_5	0·65	0·67	0·42	0·68	23	23	6	12
SO_3	0·10	0·13	0·42	0·22	4	4	6	4
CO_2	—	3·29	—	—	—	—	—	—
S	0·11	—	—	—	—	—	—	—

L. J. S.

[The Sacramento Mountains Meteorite.] By WARREN M. FOOTE (*Amer. J. Sci.*, 1897, [iv], 3, 65—66).—This iron, which has been found in the Sacramento Mountains, Eddy Co., New Mexico, weighs 237 kilos., and measures 80 × 60 × 20 cm. On the surface are the usual characteristic markings and pittings, and the Widmanstätten figures are exceptionally regular and distinct. The latter distinguish this iron from the El Capitan iron, found in 1893 about 90 miles north of the Sacramento range. As there is an entire absence of surface alteration the iron must have fallen at a comparatively recent date, and it is probably the meteor seen to fall in 1876. Analysis gave Fe, 91·39; M, 7·86; Co, 0·52; Total, 99·77. L. J. S.

[Water] from Chichan-Kanab, Yucatan. By JAS. LEWIS HOWE, and H. D. CAMPBELL (*Amer. J. Sci.*, 1896, [iv], 2, 413—415)—The Chichan-Kanab (little sea) is an almost unknown lake, over 6 leagues in length, in the interior of the peninsula of Yucatan. Water from near the shore of the lake gave analysis I, in grams per litre; that from the centre of the lake gave II.

	Ca.	Mg.	K.	Na.	SO_4.	Cl.	H_2S.
I.	0·865	0·313	0·025	0·301	3·361	0·368	—
II.	0·600	0·325	0·019	0·533	2·607	0·362	0·0495

The water near the shore is thus richer in calcium sulphate than that at the centre of the lake. Samples of material from the shores of the lake consist of gypsum. L. J. S.

Physiological Chemistry.

The Causes of Absorption of Oxygen by the Lungs. By J. LORRAIN SMITH and JOHN S. HALDANE (*Proc. physiol. Soc.*, 1896—1897, 16).—The normal oxygen tension of arterial blood varies from 35 to 66 per cent. of an atmosphere in different animals, but is nearly always higher than that in the alveoli. It rises and falls with rise and fall of the oxygen tension of the inspired air. It falls with a fall of body temperature. When the oxygen supply of the body is in-

sufficient, the oxygen tension of the blood leaving the lungs rises relatively to that of the alveolar air and may become three or four times as high. Assuming that hæmoglobin has the same properties inside and outside the body, the symptoms caused by diminished atmospheric pressure, or deficiency of oxygen in the inspired air, are not due to the hæmoglobin passing through the lungs being insufficiently saturated with oxygen. W. D. H.

Elimination of Water and Carbonic Anhydride from the Skin. By WAKELIN BARRATT (*J. Physiol.*, 1897, **21**, 192—208; *Proc. physiol. Soc.*, 1896—1897, 10—12).—The output of carbonic anhydride from the skin is small compared with that of water; the ratio for the upper limb at 35° is 1 : 200. There are variations from day to day, and from hour to hour. At 35°, the elimination of carbonic anhydride is greater than at 25°; the effect of temperature on the elimination of water is not marked.

The application of a ligature to the limb causes an increase in the carbonic anhydride and a decrease in the water eliminated.

W. D. H.

Influence of Great Altitude on the Formation of Hæmoglobin. By J. WEISS (*Zeit. physiol. Chem.*, 1897, **22**, 526—527).—The experiments were made on rabbits at Andermatt and Pilatus. Control experiments were carried out on animals of the same litters kept at Basle. There was an increase in the number of corpuscles (from 12—24 per cent.), but none in the hæmoglobin. There is no ground for attributing a beneficial influence of high altitudes to the assimilation of iron and formation of hæmoglobin. W. D. H.

Influence of Inanition on the Bones and Teeth. By HUGO WEISKE (*Zeit. physiol. Chem.*, 1897, **22**, 485—499).—The experiments were made on rabbits. After starvation, there is a slight loss of weight in the bones, which falls equally on their organic and inorganic constituents. In the teeth, on the other hand, the loss falls principally on their organic constituents. W. D. H.

A Diffusion Apparatus. By E. WAYMOUTH REID (*J. Physiol.*, 1897, **21**, 85—100).—The apparatus described and figured is for the purpose of determining the relative diffusibilities through parchment paper of substances (glucose and peptone) normally absorbed in the intestine under conditions of temperature, pressure, &c., analogous to those in the body. These experiments were made with a view of comparing the numbers with those obtained in the gut of the living animal. The same paper can be used over again for glucose, but proteid solutions affect its permeability. Grübler's peptone is twice as diffusible as Witte's, and glucose is 3·74 times more diffusible than Grübler's peptone. W. D. H.

Amount of Nucleon in Human Muscles. By MARTIN MÜLLER (*Zeit. physiol. Chem.*, 1897, **22**, 561—566).—The amount of nucleon (phosphorcarnic acid) found in the muscles of human adults in these experiments was 0·11, 0·13, and 0·22 per cent. It is less in the muscles of the new born; in five experiments, the results were: 0·04; 0·06; 0·02; 0·00; and 0·01 per cent. W. D. H.

Influence of Fat in the Food on Milk. By HENRY WING (*Ann. Agronom.*, 1896, **22**, 94—95; from *Cornell Univ. Agric. Exp. Stat. Bulletin*, 1895).—The addition of fat to the fodder of cows increases neither the quantity of milk secreted nor the amount of fat in the milk.

W. D. H.

Amount of Nucleon in Cow's, Human, and Goat's Milk. By KARL WITTMAACK (*Zeit. physiol. Chem.*, 1897, **22**, 567—574).—In cow's milk, the percentage of nucleon (phosphorcarnic acid) averaged 0·056; in human milk, 0·124; in goat's milk, 0·11. W. D. H.

Phosphorus in Human and Cow's Milk. By MAX A. SIEGFRIED (*Zeit. physiol. Chem.*, 1897, **22**, 575—578).—In cow's milk, the phosphorus of the nucleon accounts for only 6 per cent. of the total phosphorus; in human milk, where the nucleon is twice as abundant (see Wittmaack, preceding abstract), it accounts for 41·5 per cent. of the total phosphorus. The rest of the phosphorus in human milk is in the casein; there is practically no inorganic phosphorus.

W. D. H.

Action of Acids and Alkalis on the Electrotonic Currents of Nerve. By AUGUSTUS D. WALLER (*Proc. physiol. Soc.*, 1896—1897, 6—9).—The typical effect of acids is to augment the catelectrotonic and diminish the anelectrotonic current. Alkalis produce the opposite effect. W. D. H.

Deep and Surface Temperature of the Body after Section of the Spinal Cord. By MARCUS S. PEMBREY (*Proc. physiol. Soc.*, 1896—1897, 13—15).—The observations were made on a patient in whom the cord had been crushed. The surface temperature of the paralysed parts was high, even when the deep temperature was subnormal. The paralysed parts were dry compared with the non-paralysed portions of the body. W. D. H.

Effect of a Meal on the Nitrogen of the Urine. By OTTO VERAGUTT (*J. Physiol.*, 1897, **21**, 112—125).—After a meal rich in proteids, the output of nitrogen in the urine shows three rises, one immediately, the second 2 to 4 hours, and the third 6 to 7 hours later. If the food is poor in proteids, the three rises are still seen, but are not so well defined. The first rise is the most constant. Residence at 1000 metres above sea-level makes no difference in the result.

W. D. H.

The Yellow Pigment of Urine. By ARCHIBALD E. GARROD (*J. Physiol.*, 1897, **21**, 190—191).—Riva and Chiodera have stated that the action of potassium permanganate on urobilin is to convert it partially into a substance which has the characters of the yellow pigment of urine.

Conversely, in the present paper it is shown that the action of pure aldehyde on the yellow pigment (in neutral alcoholic solution) is to convert it very largely into a substance with the characters of urobilin.

The yellow pigment does not necessarily come, however, ultimately

from the bile pigment, but also, and perhaps primarily, from the blood pigment, urobilin being in each case an intermediate substance.

W. D. H.

Albumosuria. By KARL H. HUPPERT (*Zeit. physiol. Chem.*, 1897, **22**, 500—507).—Some years ago Noël-Paton (Abstr., 1893, ii, 290) described a crystalline proteid occurring in human urine. Crystallisation occurred spontaneously in the urine on standing, and the proteid was recrystallised after its separation from the urine by the use of ammonium sulphate. The present article points out that this proteid, which Noël-Paton considered to be a globulin, is probably heteroalbumose. The principal ground on which this conclusion is based is the concordance in its ultimate analysis with that of albumoses in other cases of albumosuria, and with that of Kühne's heteroalbumose.

W. D. H.

Fibrinuria. By DAVID M. GREIG (*J. Pathol. and Bacteriol.*, 1897, **4**, 401—403).—The occurrence of urine which deposits a clot of fibrin on standing is a rare condition. The details of such a case are described; temporary congestion of the kidneys led apparently to an exudation of blood plasma, and this formed the source of the fibrin.

W. D. H.

Multiple Intestinal Concretions in Man. By CARL TH. MÖRNER (*Zeit. physiol. Chem.*, 1897, **22**, 522—525).—The concretions removed from the intestine of a man gave the following result on analysis:

Magnesium ammonium phosphate	82·23	per cent.
Calcium phosphate	5·24	,,
Magnesium phosphate	1·64	,,
Calcium carbonate	1·61	,,
Calcium soap	0·75	,,
Neutral fat	0·20	,,
Insoluble organic substance	1·90	,,
Water traces of soluble organic substances, &c.	6·43	,,

W. D. H.

Chlorides and Phosphates of the Blood in Disease. By WACLAW VON MORACZEWSKI (*Virchow's Archiv.*, 1896, **146**, 424—452). —The blood was investigated in a number of diseased conditions of diverse kinds. Clinical and chemical details are given in each case. In pneumonia, the chlorides are diminished; they rise after the crisis. The phosphates are abundant; this is usual in acute diseases, the urine showing a correspondence. In nephritis, there is an increase in the chlorides and a decrease in the phosphates. In lead poisoning, if lead is passing into the urine, the blood is rich in chlorides. The urine is poor in chlorides, rich in phosphates, the opposite to the blood; the same is true for anæmia. W. D. H.

Physiological Action of Nitrites. By JOHN S. HALDANE, R. H. MAKGILL, and A. E. MAVROGORDATO (*J. Physiol.*, 1897, **21**, 160—189). —A full account of experiments of which a preliminary notice has already appeared (this vol., ii, 63). W. D. H.

Physiological Action of Choline, Neurine, and Allied Substances. By FREDERICK WALKER MOTT, and WILLIAM D. HALLIBURTON (*Proc. physiol. Soc.*, 1896—1897, 18—20).—When injected into the circulation, small doses of choline hydrochloride cause a marked temporary fall of blood pressure, which is cardiac, and not peripheral in origin. It occurs also after section of the vagi. Neurine hydrochloride produces a preliminary fall and a subsequent rise of pressure, respiration being slowed and deepened. This drug is more toxic than choline, less than a decigram being the fatal dose in a dog; respiration ceases before the heart.

The physiological interest of these observations is derived from the fact that the cerebrospinal fluid, in cases of brain disease, where, as in general paralysis of the insane, there is great wasting of the brain substance and disintegration of its cells, produces exactly the same effects as solutions of choline. Normal cerebrospinal fluid is innocuous; the toxicity of the pathological fluid is due to some non-proteid substance precipitable by phosphotungstic acid. It is probable that this substance is choline, derived from the lecithin of the brain. If this is the case, the enfeebled circulation with severe fainting fits and fatty degeneration of the heart, so frequently seen in cases of general paralysis, will be in part accounted for. The blood removed by venesection from patients during the fits contains the same substance.

W. D. H.

Physiological Action of Hydrastine Hydrochloride. By CHARLES D. F. PHILLIPS and MARCUS S. PEMBREY (*Proc. physiol. Soc.*, 1896—1897, 4—6).—The effect of hydrastine hydrochloride on the various systems is described in detail; the most marked effect is convulsions similar to those produced by strychnine. The drug is used as an abortefacient, and the present experiments on cats confirm this; it, however, at the same time kills the offspring. W. D. H.

Fermented Fish. By CARL TH. MÖRNER (*Zeit. physiol. Chem.*, 1897, **22**, 514—521).—In some parts of northern Sweden, fish are loosely packed in casks with a little salt, the casks are closed, and allowed to remain for some weeks. The fish, therefore, is eaten in what is practically a putrefied condition. The gases obtained were carbonic anhydride, hydrogen sulphide, and vapour of methyl mercaptan. Succinic acid is abundant, and so are both volatile, and solid fatty acids. Ammonia, methylamine, dimethylamine, trimethylamine, and choline were found among the bases. Leucine is present in abundance, and ethylic alcohol and acetone in small quantities. Tyrosine, indole, scatole, phenol, putrescin and cadaverine are absent.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Butylic Alcohol Fermentation. By OSKAR EMMERLING (*Ber.*, 1897, **30**, 451—453).—After repeated attempts to isolate Fitz's "*Bacillus butylicus*," a variety of hay, obtained from Alsace, was ultimately found to yield this organism.

The pure bacillus quickly sets up butylic alcohol fermentation in glycerol, producing from 100 grams of glycerol, 6·3 grams of pure normal butylic alcohol, and from 100 grams of mannitol, 10·5 grams of butylic alcohol. Comparison with Beyerinck's "*Granulobacter butylicum*" showed that the latter produced no trace of butylic alcohol from glycerol, although it gave it with grape sugar; it is not identical, therefore, with Fitz's bacillus.

On distilling the product of the action of the bacillus on grape-sugar, a small quantity of a solid substance melting at 60°, probably palmitic acid, passes over along with the ethylic alcohol and steam.

J. F. T.

The Changes which take place in Milk, either Spontaneously or during Culinary Processes. By ANTOINE BÉCHAMP (*Bull. Soc. Chim.*, 1896, [iii], **15**, 426—455. See this vol., 113, 183).—A continuation of an historical review of the subject. M. W. T.

Fermentation produced by Moulds. By OSKAR EMMERLING (*Ber.*, 1897, **30**, 454—455).—By the action of *Mucor racemosus* on 100 grams of cane-sugar in a solution containing 2 grams of potassium phosphate, 1 gram of magnesium sulphate, and 5 grams of potassium nitrate in 1500 grams of water, large quantities of carbonic anhydride are produced, together with 1·46 per cent. of ethylic alcohol and 0·31 gram of pure succinic acid, the latter being isolated by means of its lead salt. On extracting the filtrate from the lead salt with alcohol and evaporating, 1·83 gram of glycerol (identified by means of the acraldehyde reaction) were obtained.

The numbers representing the relative proportions of these substances produced in this fermentation are: alcohol 22, glycerol 1·85, and succinic acid 0·31. J. F. T.

Hydrolysis of Melezitose by Soluble Ferments. By EMILE E. BOURQUELOT and H. HÉRISSEY (*J. Pharm.*, 1896, [vi], **4**, 385—387. Compare Abstr., 1896, ii, 322).—Distilled water which has been left in contact with a mature culture of *Aspergillus niger* for 3 days readily hydrolyses melezitose, most probably into *d*-glucose and touranose.

J. J. S.

Action of the Oxidising Ferment of Mushrooms on Phenols and Phenolic Ethers. By EMILE E. BOURQUELOT (*J. Pharm.*, 1896, [vi], **4**, 241—248, and 440—447. Compare Abstr., 1896, ii, 383, and this vol., ii, 66).—The oxidising ferment is best obtained from *Russula delica*, or, in default of this, from *Lactarius velutinus*, Bert., or *L. vellereus*, Fr., but the latter yield less active solutions.

Phenol, in a slightly alkaline solution, is readily oxidised by the ferment. Quinol, pyrogallol, and its isomerides are also readily oxidised. Phloroglucinol, however, is oxidised but slowly. Anisoil and phenetoil, in aqueous alcohol, are readily oxidised; also guaiacol. The latter is not merely coloured by the oxidising ferment of mushrooms, but also by ferments from numerous phanerogams. The red colour produced on guaiacol can be changed to blue by adding α-naphthol in aqueous alcohol. Acetylguaiacol and veratrole give yellowish-red precipitates; a solution of creosol first changes to green, and then becomes reddish-yellow, but, on shaking, it again turns green; finally, a yellowish

precipitate is formed. Acetyleugenol behaves in much the same way as eugenol. Vanillin, in 1 per cent. aqueous solution, gives a voluminous precipitate, and the reaction proceeds more readily in the presence of a little acid. Vanillic acid acts in much the same way.

J. J. S.

Selection of Organic Nutritive Substances. By WILHELM PFEFFER (*Bied Centr.*, 1896, **25**, 813—814; from *Pringheim's Jahrb.*, 1895, **28**, 205—268; and *Bot. Centr.*, 1896, **65**, 202).—In experiments with *Aspergillus niger* grown in a solution containing glycerol (1 per cent.) and dextrose (6 per cent.), it was found that the glycerol was not attacked, whilst with 2 per cent. dextrose and 7·3 per cent. glycerol, the dextrose was entirely consumed. *Penicillium* utilises glycerol in relatively large amounts. Lactic acid also is not attacked in presence of dextrose, whilst acetic acid is utilised in greater quantity than dextrose when they are present together. Small quantities of dextrose in presence of much peptone are entirely consumed. Both fungi attack dextro- and lævo-tartaric acids, but prefer the former. *Aspergillus flavescens*, and *Monilia candida* behave similarly, whilst *Aspergillus fumigatus*, *Mortierella reticulata*, *Saccharomyces ellipsoideus*, "rose yeast," "Levure de Duclaux," and *B. subtilis* utilise both acids equally.

Lævo-tartaric acid is an unsuitable food for such fungi as prefer the dextro-acid, but suitable for those which do not split up racemic acid.

As regards the relation between the nutritive value of organic substances and their chemical constitution, there is no definite rule; compounds very similarly constituted may have very different food values, and *vice versa*. The nutritive value also cannot be judged by the heats of combustion, which are, for example, identical in the case of the optical antipodes, which are frequently physiologically different.

The relative food value is generally estimated from the rate of development under equal conditions. The author also determined the amounts of dry fungus obtained by the consumption of 100 parts of nutritive matter. The relation is called the economic coefficient. In the case of *Aspergillus niger*, the following economic coefficients were obtained: glycerol = 20; dextrose = 43. With *Penicillium glaucum*, glycerol = 20; dextrose = 33.

Aspergillus niger, beer yeast, and *Saccharomyces ellipsoideus* in no case attacked mandelic acid. *Penicillium glaucum* behaved differently. Yeasts which split up racemic acid, seemed to prefer dextromandelic acid, whilst lævo-mandelic acid was chiefly consumed when inoculated with a mixture of putrefying bacteria.

N. H. J. M.

Crystallisation of Xanthophyll (Carotin) and Proof of its Presence in Leaves. By HANS MOLISCH (*Chem. Centr.*, 1896, i, 815—816; from *Ber. deut. bot. Ges.*, **14**, 18—28).—The author's 'potash' method of separating chlorophyll and xanthophyll in leaves is as follows. The fresh green leaves, either whole or in small pieces, are immersed in dilute alcohol containing 40 per cent. of alcohol by volume, and in which 20 per cent. by weight of potassium hydroxide is dissolved, and left in closed vessels in the dark until all the chlorophyll has been extracted. In many cases, one day suffices for the complete extraction of the chlorophyll, the whole of the xanthophyll

remaining in the leaves. After washing with water, the leaves are immersed in glycerol. Every cell which formerly contained chlorophyll is now seen under the microscope to contain crystals of xanthophyll; and whilst the epidermis and vascular bundles are free from these crystals, the assimilation parenchyma appears impregnated with them. In some few cases, the xanthophyll separates in yellow drops, or permeates the whole of the cell content. The crystals vary from yellowish to brownish orange, and exhibit a most remarkable nacreous lustre. Crystallographic examinations were made with the leaves of *Mimulus moschatus*, Dougl.; *Polygonum tinctorium*, L.; *Mercurialis annua*, L., and an etiolated leaf of wheat. The xanthophyll crystals obtained from *Viola odorata* have the form of very long, narrow tables. Their optical properties indicate that they belong to the rhombic system. Unmistakable differences in the crystals from various crystallisations render it improbable that they are all identical. They are soluble in ether, absolute alcohol, chloroform, carbon bisulphide, glacial acetic acid, and concentrated solution of chloral hydrate, but insoluble in dilute acids and alkalis, and in water and glycerol. With concentrated sulphuric acid or nitric acid, the crystals become indigo-blue, turning quickly yellow, however, in the latter case. Bromine water or vapour causes a fugitive blue coloration, and then the crystals become colourless.

With concentrated hydrochloric acid and phenol or thymol, the crystals, after a short time, become deep blue. In iodised chloral hydrate, they turn dirty green. All these reactions are best shown with leaves which have been freed as far as possible from water.

The author does not attempt to decide whether the crystals formed in this reaction are all xanthophyll or all carotin crystals, or whether these are identical or whether they consist in part of colouring matters nearly related to carotene. He names them all carotin, and understands by that term a group of closely-related colouring matters which are analogous to the colouring matter contained in the carrot. He has attempted to prove that the crystals are not coloured cholesterol crystals. E. W. W.

Colouring Matters contained in Leaves, and the Relationship of Chlorophyll to the Colouring Matter of Blood. By W. O. ALEXANDER TSCHIRCH (*Chem. Centr.*, 1896, i, 816—817; from *Schweiz. Woch. Pharm.*, **34**, 85—87).—The yellow-colouring matter of leaves and probably that also of flowers, is a mixture of xanthocarotin, whose solution shows three absorption bands in the violet, and xanthophyll, whose solution exhibits no bands, but absorbs the ultra violet rays (end-absorption). Both compounds were obtained in a crystalline form, and neither contains nitrogen. The chlorophyll of living leaves is probably the product of the union of two other compounds of which one is phyllocyanin, and the other a colourless compound of unknown composition. Phyllocyanin and its compounds exhibit absorption spectra, of which only two of the five bands seen in the visible part of the spectrum agree with those of the oxyhæmoglobin of blood. By employing a quartz spectroscope, the author has detected a new band at the end of the violet which agrees exactly with the principal absorption band of blood observed by Soret, resembling it also in its constancy

of position, which varies only between the lines G and M. The reddish yellow crystals of phyllopurpuric acid obtained from alkaline solutions of chlorophyll, that is, from salts of chlorophyllic acid, exhibit essentially the same spectrum, in the visible part of the spectrum, as the red hæmatoporphyrin prepared by Nencki from blood. The solutions of both show a red fluorescence.

Assuming that similarity of absorption spectra is indicative of similarity of atomic constitution, then chlorophyll must be nearly allied to the colouring matter of blood. Moreover, both series of compounds, on distillation with zinc, yield pyrroline, hence both evidently contain the pyrroline ring.

The quartz spectroscope employed by the author contained a quartz doublet lens in the collimator tube, and in place of the telescope a quartz lens. The prism was a Cornu prism composed of dextro- and lævorotatory quartz. The containing vessels were also of quartz, and the heliostat had a German-silver mirror. With this apparatus, the solar spectrum as far as the Fraunhofer line U could be photographed so that the additional portion of the spectrum was longer than the ordinary visible portion. Many phenomena hitherto named end-absorptions were found to consist of bands. E. W. W.

The Supply of Soil Nitrogen. By EUGEN W. HILGARD (*Ann. Rep. Agric. Exper. Stat. Univ. California* for 1894—1895, 32—35).—Experiments were made to discover a plant suitable for the climate of California, for the purpose of green manuring, especially for orchards. It has been noticed that, when orchards have been carefully weeded for a number of years, their production decreases, notwithstanding the application of manures ; the soil, moreover, deteriorates physically. A leguminous plant, *Tetragonolobus purpureus*, for which the name "square-pod pea" is proposed, seems likely to be suitable. It yields 24—26 tons per acre (equivalent to about 5 tons of hay). Its nitrogen percentage is less than that of lucerne or clover, but the nitrogen of the produce of an acre would be much greater. If sown in January, it could be ploughed in by the middle of May.

The alkali soils of California contain in the first 12 inches as much as 0·33 per cent. of soluble salts, consisting mainly of sodium chloride and sulphate, but containing no less than 12 per cent. of nitrate. This corresponds with 1400 lbs. of sodium nitrate per acre in the first 12 inches of soil. N. H. J. M.

Distribution of the Salts in Alkali Soils. By EUGEN W. HILGARD and ROBERT H. LOUGHRIDGE (*Ann. Rep. Agric. Exper. Stat. Univ. California* for 1894—1895, 37—71).—Under ordinary circumstances, the alkali soils of California yield very heavy crops, or nothing at all, according to whether there is a heavy rainfall or not. With irrigation, good crops are certain for some years, after which, owing to evaporation and the consequent rise of alkali to the surface, the land becomes worse than before. The following numbers show the amounts of soluble salts (in lbs. per acre) in the soil and subsoil of unirrigated land, bearing natural vegetation.

	Sodium. Nitrate.	Sodium. Chloride.	Sodium. Carbonate.	Alkali. Sulphates.	Total.
1st 12 inches	20	190	230	370	810
2nd "	—	190	4140	730	4460
3rd "	—	1040	13590	2450	17080
4th "	—	20	4040	620	4680

The results are important as showing that the greater amount of the salts are not far from the surface, and that the amount is limited. The land can therefore be completely cured by underdrainage.

The application of gypsum (1·5 tons per acre) gives very good results with barley on land which was otherwise sterile. It was found that the percentage of sodium carbonate was greatly reduced at the surface, and even, though to a less extent, in the subsoil. The application of gypsum also had the effect of liberating potash from the zeolites of the soil, giving rise to an increase of potassium sulphate in the first 6 inches of soil. The nitrates were also increased.

In order to check evaporation, the land should be deeply tilled, and to enable the deep tilth to be maintained, crops should be grown which allow hoeing. This is, however, impossible in the case of "black" alkali soils; these must be treated with gypsum some time before sowing, after which irrigation may be necessary. N. H. J. M.

Growing Sugar Beets on Alkali Soils. By EUGEN W. HILGARD and ROBERT H. LOUGHRIDGE (*Ann. Rep. Agric. Exp. Stat. Univ. California* for 1894—1895, 71—91). Sugar beet of good quality can be grown on land containing as much as 12,000 lbs. of alkali salts per acre to the depth of 3 feet, provided that the amount of sodium chloride does not exceed 0·04 per cent. or 1,500 lbs. per acre. Carbonates are much less injurious than chlorides, and probably not more injurious to the quality of the roots than sulphates. The maximum amounts of carbonates and sulphates, when good roots were obtained, were respectively about 4,000 lbs. and 9,000 lbs. per acre in the first 3 or 4 feet of soil.

The appearance of a soil is not a sufficient guide, since compact soils show an efflorescence quite out of proportion to the small amount of alkali present, whilst loose soils, which show very little efflorescence, may contain excessive amounts of soluble salts. N. H. J. M.

Diminution of the Nitrogenous Matter in Wheat in the Department of Nord. By BALLAND (*Compt. rend.*, 1897, **124**, 158—159).—Eight samples of wheat grown in the Département du Nord, and analysed by Millon in 1848, contained from 10·23 to 13·02 per cent. of proteids in the normal condition, and 12·32 to 15·44 per cent. when dry. Six samples of wheat grown in the same locality in 1895, two in 1890, and one in 1887 were found by the author to contain from 8·96 to 10·62 per cent. of proteids in the normal state, and 10·36—12·51 per cent. when dry. Wheat now grown in Algeria contains the same percentage of proteids as the Algerian wheats examined by Millon. The yield per hectare in Algeria remains practically what it was in 1852, but that in the Département du Nord has been increased from about 14 hectolitres por hectare to 28 hectolitres. Schlœsing has shown that the proportion of proteids in wheat depends

on the richness of the soil in nitrogen, and the author suggests that a gradual exhaustion of the nitrogen in the soil explains the diminution observed in the wheat of the Département du Nord. C. H. B.

Value of Creamery Separator Skim Milk for Pig Feeding. By WILLIAM A. HENRY (*Ann. Rep. Agric. Exper. Stat. Univ. Wisconsin*, No. 12, for year ending June, 1895, 7—72).—A number of experiments are described in which pigs were fed with maize meal alone, and with maize meal together with different amounts of skim milk. The following average results show the weights (in lbs.) of meal and skim milk required to produce 100 lbs. gain in live weight.

	Maize meal.	Skim milk.
Grain alone	506	—
Meal 1 lb. to skim milk 1—3 lbs. ...	321	585
" " " " 3—5 " ...	265	1048
" " " " 5—7 " ...	250	1434
" " " " 7—9 " ...	207	1616

Taking the averages of all the experiments, it is seen that 462 lbs. of skim milk saved 100 lbs. of meal, the largest saving being when 1—3 lbs. of skim milk is used for each lb. of meal.

The chief value in the utilisation of skim milk is not, however, in saving meal, but in maintaining a healthy condition, and in promoting the rapid growth of the animals. N. H. J. M.

Analytical Chemistry.

Decomposition of Mercurous Chloride and the Estimation of free Chlorine. By IYOTIBHUSHAN BHADURI, *Zeit. anorg. Chem.*, 1897, 13, 407—411).—When a neutral or alkaline solution containing chloride, chlorate, hypochlorite, and free chlorine is treated with an excess of mercury, the chloride and chlorate remain unaltered, the free chlorine forms mercurous chloride, and the hypochlorite forms mercuric oxide; further, the free chlorine acting on the hypochlorite forms hypochlorous acid, and this combines with mercury to form mercuric oxychloride, which is insoluble in water. The mixed precipitate of mercury compounds is separated by filtration, carefully washed, and then treated with a very slight excess of dilute hydrochloric acid. Mercurous chloride and free mercury remain undissolved. The quantity of mercuric chloride dissolved by the hydrochloric acid gives the quantity of hypochlorous acid, and the free chlorine is represented by the mercurous chloride. The chlorine in the latter compound is estimated by titration with alkali; but, in order to obtain correct results, it is necessary to boil the mixture for about 15 minutes, and, after allowing it to cool, to collect the residue, treat it again with alkali, collect and wash. The chlorine in the filtrates is estimated by means of silver nitrate, after acidification with nitric acid. E. C. R.

Estimation of Oxygen in the Air and in Aqueous Solution. By D. ALBERT KREIDER (*Zeit. anorg. Chem.*, 1897, 13, 418—426; also *Am. J. Sci.*, [iv], 2, 361—367).—The method consists in treating a

measured volume of air with strong hydriodic acid in the presence of nitric oxide, then neutralising the acid with potassium hydrogen carbonate and estimating the liberated iodine by means of N/10 arsenious acid. This method is similar to the one employed for the estimation of perchlorate previously described (Abstr., 1896, ii, 123); and the same precautions must be taken to exclude the air. 100 c.c. of air, calculated at 0° and 760 mm., is taken for each experiment, and the best quantity of nitric oxide to employ is 15 c.c. The results are accurate to 0·05 per cent.

It is proposed to estimate the oxygen dissolved in water in a similar manner; each experiment takes only about 10 minutes. The mean of the results gives 6·022 c.c. of oxygen in 1000 c.c. of distilled water at 20° and 760 mm.

A full description of the apparatus employed is given.

E. C. R.

Estimation of Organic and Ammoniacal Nitrogen. By AIMÉ PAGNOUL (*Ann. Agron.*, 1896, **22**, 543—544).—The following modification of Kjeldahl's method is recommended. The substance (0·5—1 gram; or, if soil, 10 grams) is boiled with sulphuric acid (25 c.c.) and a drop of mercury; less than an hour is usually sufficient. The mixture is then poured into a flask with 200 c.c. of water, caustic soda solution (40 c.c.), is added, and the whole cooled. Zinc dust (about 1 gram), caustic soda (40 c.c.), and potassium sulphide (6 c.c.) are quickly added, and the distillation proceeded with. The condenser is a long tube which dips into acid of known strength; it is connected with the flask by means of a tin tube. To prevent the acid from getting too hot, the receiver is placed in a vessel containing cold water.

If the substance to be analysed contains nitrates, it is boiled for a short time with a few c.c. of ferrous chloride and hydrochloric acid before the sulphuric acid is added.

The caustic soda solution employed is prepared by heating soda-lime (1 kilo.) with distilled water (1 litre). The object of adding it in two separate portions to the acid is to avoid heating, and consequent possible loss of ammonia, before distilling. The sulphide solution contains potassium sulphide (200 grams), and caustic potash (100 grams per litre); of this solution, 6 c.c. suffices when 0·8 gram of mercury is employed.

N. H. J. M.

Estimation of Nitrogen in Guano. By E. FRANKE (*Chem. Zeit.*, 1896, **20**, 325—326).—Haselhoff has recommended that 5 grams of the guano should be extracted with water on a filter, the filtrate made up to 250 c.c., and the joint ammonia and nitric nitrogen estimated by Ulsch's process in 25 c.c. of the liquid (0·5 gram of the sample). The insoluble matter on the filter is then treated by Kjeldahl's method.

The author finds that the results obtained by this method are very seriously below the truth; this is, no doubt, due to the presence of nitrogenous organic matters soluble in water, but which are imperfectly decomposed by boiling with aqueous soda. The final conclusions are (1) that Jodlbaur's phenol sulphuric acid process works very well with samples of guano if they do not contain more than 2 per cent. of

nitre; (2) that the results are satisfactory if the guano is first treated in the manner directed by Ulsch (reduction with iron and sulphuric acid), and then at once by Kjeldahl's process. L. DE K.

Analysis of Sodium Nitrate. By AIMÉ PAGNOUL (*Ann. Agron.*, 1896, **22**, 541—543).—Analyses of sodium nitrate by Schlœsing's method are liable to an error of 1 per cent. or more. The indirect method in which the chlorine, sulphates, moisture, and insoluble matter are determined, and the nitrate estimated by difference, is a longer process but gives better results. Even an error of 10 per cent. in each determination (and in the same direction) will only give an error of less than 0·5 per cent. in the case of 96 per cent. sodium nitrate. Moreover, the exact nature of the impurity is ascertained by the indirect method.

In Schlœsing's method, a correction is necessary, especially when only small quantities of gas are obtained (as in water and soil analysis), as the gas is never completely absorbable by ferrous chloride. In order to make this correction, a graduated tube is employed, so constructed that a few c.c. of a mixture of ferrous chloride and hydrochloric acid can be admitted. After absorption, the residual gas is measured.

N. H. J. M.

Sensitive Test for Nitrous Acid. By E. RIEGLER (*Zeit. anal. Chem.*, 1896, **35**, 677—678).—To 5—6 c.c. of the liquid add 0·02—0·03 gram of crystallised 1 : 4-naphthylaminesulphonic acid, and shake well. Then add 2 or 3 drops of concentrated hydrochloric acid and shake again vigorously for a minute. Then pour upon the surface 20—30 drops of ammonia. At the surface of contact of the liquids, a rose colour will be developed, which is best observed by transmitted light.

M. J. S.

Estimation of Citrate-soluble Phosphoric Acid by means of Molybdate Solution. By MAX SCHMOEGER (*Chem. Zeit.*, 1896, **20**, 497—498).—Koenig has stated that citric acid, when present in excess, such as is the case when dealing with citrate-soluble phosphoric acid, entirely, or partially, prevents the precipitation of the phosphoric acid by means of molybdate solution. The author, on the other hand, finds that the phosphoric acid is completely precipitated.

If, to save trouble, magnesium mixture is added directly to the citric acid solution from basic slags, the phosphoric acid is also completely precipitated, but the precipitate is contaminated with silica; this may, however, be subsequently separated by means of hydrochloric acid in the usual way. L. DE K.

Estimation of Citrate-Soluble Phosphoric Acid in Basic Slags by means of Citric Acid. By MAX PASSON (*Zeit. angw. Chem.*, 1896, 677—678).—The author (Abstr., 1896, ii, 575) has modified his process so as to obtain a stronger solution which gives no trouble in the further stage of the manipulation. Ten grams of the sample is exhausted with half a litre of a 2·8 per cent. solution of citric acid for half an hour in a rotating apparatus; 75 c.c. of the filtrate is then boiled in a 300 c.c. flask with 20 c.c. of nitric acid, 15 c.c. of sulphuric acid, and a drop of mercury until the organic

matter has been destroyed, and, after adding 20 c.c. of a 10 per cent. brine, the liquid is made up to the mark, and 100 c.c. of the filtrate is treated by the molybdate or magnesia citrate process. L. DE K.

Valuation of Borax. By J. GEORGE HEID (*Zeit. angw. Chemie*, 1896, 679).—The following process is recommended. Ten grams of the sample is dissolved in water and made up to 250 c.c.; the chlorine in 125 c.c. of this solution is precipitated by means of nitric acid and silver nitrate, and after weighing the silver chloride, the corresponding amount of sodium chloride is calculated. 25 c.c. of the solution is mixed with excess of hydrochloric acid and evaporated to complete dryness on the water-bath, the residue dissolved in water, and the chlorine precipitated as before. The difference between the two results gives the amount of sodium chloride corresponding with the borax present. If, to save time, a volumetric estimation of the chlorine is preferred, the dry mass, before dissolving it in water, must be repeatedly extracted with absolute alcohol to remove the boric acid. L. DE K.

Organic Analysis by Analysis of the Gases produced in the Berthelot Calorimetric Bomb. By NATHAN ZUNTZ and JOH. FRENTZEL (*Ber.*, 1897, **30**, 380—382).—The authors propose to carry out an organic analysis at the same time as a determination of the heat of combustion, especially with samples of food-stuffs, manures, &c. For this purpose, the bomb is weighed after the introduction of the oxygen, of which the composition is found by careful analyses. At the close of the combustion, samples of the gas contained in the bomb are analysed, and the total weight of the gas is found by deducting the weight of the water and nitric or other acid which is formed, together with the ash of the substance, from the sum of the weights of the gas put into the bomb, and of the substance taken. The results as regards carbon and hydrogen are satisfactory, whilst as regards nitrogen they are less so. No analyses are quoted.

A. H.

Estimation of Potassium. By ALBERT PRAGER (*Chem. Zeit.*, 1896, **20**, 269. Compare this vol., ii, 160).—The author states that when potassium chloride in dilute solution is slowly evaporated with platinic chloride, the platinochloride formed is more crystalline and purer than the product obtained in the usual way.

The following process is recommended for the analysis of compounds containing the potassium as sulphate. The solution is carefully precipitated with barium chloride, excess being avoided, and the filtrate is diluted to 75 c.c.; after adding the solution of platinic chloride, the mixture is evaporated on the water-bath, which should not boil, until the surface becomes covered with crystals; it is then allowed to cool, and when cold the evaporation is again continued until about 5 c.c. of liquid is left. When cold, 20 c.c. of 96 per cent. alcohol is added, and the precipitate washed, on a weighed filter with 80 per cent. alcohol and finally dried at 110°. As some kinds of filter paper contain matters soluble in alcohol and water, the author advises washing the filter before weighing, first with alcohol and then with hot water, drying finally at 110°. L. DE K.

Estimation of Potassium. By FREDERICK T. B. DUPRÉ (*Chem. Zeit.*, 1896, **20**, 305).—Ruer (this vol., ii, 160) has proposed to calculate the amount of potassium chloride from the platinochloride by multiplying by 0·304 instead of 0·3056, the factor proposed by Fresenius. The author states that the latter is absolutely correct if Fresenius's instructions are carefully followed, but it is not possible to get potassium platinochloride in such a state of purity that it absolutely corresponds with the formula; different methods of analysis, therefore, require different factors. L. DE K.

Estimation of Lime in Raw Materials used for Cement-making. By FRITZ KLUGE (*Chem. Zeit.*, 1896, **20**, 372).—Two grams of the finely-powdered sample, after being heated in a platinum crucible, over the blow-pipe, for about 10 minutes, is weighed, removed from the crucible and boiled with 50 c.c. of water; 40 c.c. of standard sulphuric acid is next added, and the excess of acid titrated with standard potash using phenolphthalein as indicator.

The acid and alkali should have been checked by means of a limestone of known composition similar in quality to the stone under examination. The results are very satisfactory, and the analysis can be finished in about 20 minutes. L. DE K.

Separation of Thorium from the other Rare Earths by Potassium Nitride. By LOUIS M. DENNIS (*Zeit. anorg. Chem.*, 1897, **13**, 412—417).—A solution of potassium nitride is prepared by neutralising a dilute solution of azoimide with pure potassium hydroxide and then adding an excess of azoimide. When a solution of thorium chloride or nitrate is treated with the above solution and boiled for one minute, the thorium is quantitatively precipitated as thorium hydroxide. (Abstr., 1894, ii, 256). From a mixture of the rare earths prepared from Brazilian monazite, the thorium is also completely precipitated in a pure state, and the purity of the precipitate is independent of the relative amounts of thorium and the other rare earths.

E. C. R.

Separation of Aluminium from Iron. By FRANK A. GOOCH and F. S. HAVENS (*Zeit. anorg. Chem.*, 1897, **13**, 435—440; also *Amer. J. Sci.*, 1896, [iv], **2**, 416—420).—The method is based on the insolubility of aluminium chloride in a mixture of ether and hydrochloric acid, whereas ferric chloride is easily soluble.

A measured quantity of aluminium chloride solution (0·0761 gram Al_2O_3) was evaporated to dryness in a platinum dish, a solution of ferric chloride (0·15 gram Fe_2O_3) added; then 15 c.c. of a mixture of equal parts of strong hydrochloric acid and ether, and the mixture saturated with hydrogen chloride at 15°; a further 5 c.c. of ether was added, and the mixture again saturated with hydrogen chloride. The precipitated aluminium chloride was collected on asbestos in a filter-crucible, washed with a mixture of ether and hydrochloric acid, saturated with hydrogen chloride, and dried for half an hour at 150°; it was then heated with 1 gram of mercuric oxide, at first gently and finally over the blow-pipe, and weighed as Al_2O_3. The results were accurate. Instead of heating with mercuric oxide, the aluminium chloride may be redissolved and precipitated with

ammonia. Care must be taken that sufficient ether is present in the mixture, as otherwise the solution separates into two layers, the lower one consisting of a green, oily layer of ferric chloride dissolved in ether.

E. C. R.

Estimation of Sesquioxides in Phosphates and Superphosphates. By VON GRUEBER (*Zeit. angw. Chem.*, 1896, 741—742).—Ten grams of the sample is heated in a porcelain dish with 150 c.c. of water and 20 c.c. of hydrochloric acid, the whole evaporated to dryness, and the residue treated with dilute hydrochloric acid, filtered, if necessary, and made up to 500 c.c.

Fifty c.c. of the solution is heated in a 200 c.c. flask and nearly neutralised with 20 per cent. aqueous soda; 30 c.c. more of the soda solution is then added, and the whole boiled for ten minutes. When cold, the liquid is made up to the mark, filtered, and 100 c.c. of the filtrate slightly supersaturated with hydrochloric acid; the alumina is then precipitated as phosphate by adding a slight excess of ammonia, and boiling for a short time. The weight of the phosphate multiplied by 41·8 gives the amount of alumina in 0·5 gram of the sample.

One hundred c.c. of the solution is placed in a 250 c.c. flask, and the iron is reduced by means of metallic zinc and then estimated by means of potassium permanganate according to Fresenius's directions.

L. DE K.

Estimation of Manganese in Spiegels, &c. By H. BREARLEY (*Chem. News*, 1897, 75, 13—16).—The author, after searching investigation, adopts the following method. One to 1·5 gram of 20 per cent. spiegeleisen or a proportionate amount of other manganiferous iron is dissolved in hydrochloric acid, oxidised with nitric acid, filtered, if necessary, through a small asbestos filter, neutralised with sodium carbonate, diluted to about 900 c.c. and treated with a 3·75 per cent. solution of sodium acetate at the rate of 20 c.c. per gram of iron. It is then boiled and measured, noting the temperature; enveloped in cloth to retard cooling, and half the volume syphoned or filtered off, again noting the temperature. The liquid is cooled, neutralised with sodium carbonate, acidified slightly with acetic or sulphuric acid, then run into sufficient 0·3156 per cent. potassium permanganate solution containing 10 c.c. of 20 per cent. zinc sulphate solution, shaking constantly, allowed to settle, an aliquot part filtered off, acidified, and determined with ferrous ammonium sulphate and permanganate. Corrections being made for the variations in volume due to temperature, the calculations are as usual.

D. A. L.

Colorimetric Estimation of Iron by Means of Potassium Thiocyanate. By ARTHUR BORNTRAEGER (*Chem. Zeit.*, 1896, 20, 398—399).—The author compares the intensity of the red colour produced on adding potassium thiocyanate to the solution under examination with that obtained with an iron solution of known strength.

The method is more particularly intended for the estimation of traces of iron in the ash of wines or beers. The other salts contained in the ash do not influence the accuracy of the process.

L. DE K.

Estimation of Tin and Copper in Tin-dross. By L. Rürup (*Chem. Zeit.*, 1896, **20**, 406).—In analysing the dross formed in tin-baths for tinning iron, copper, &c., 500 grams of the well mixed sample is fused in a Hessian crucible with cream of tartar, sodium carbonate and chalk for about half an hour. The crucible, rapidly cooled, is broken, and the metallic button cleaned and weighed. About 1 gram of borings obtained from this is analysed by digesting it with 22 c.c. of nitric acid, sp. gr. 1·2, adding 10 c.c. of the concentrated acid, collecting the stannic acid produced, and converting it into stannic oxide by ignition. The filtrate is evaporated to dryness, and after dissolving the residue in dilute sulphuric acid, the copper is precipitated electrolytically. L. de K.

Use of Organic Acids for the Estimation of Vanadium. By Philip E. Browning and Richard J. Goodman (*Zeit. anorg. Chem.*, 1897, **13**, 427—434; also *Amer. J. Sci.*, [iv], **2**, 355—360).—The authors have examined the applicability to the estimation of vanadium of the method described by Browning (Abstr., 1894, 483) which consists in reducing vanadic acid to vanadium tetroxide by boiling with tartaric acid, and then titrating with iodine. When estimating vanadium by this method in the presence of molybdenum and tungsten, the presence of sodium tungstate does not affect the results; ammonium molybdate is, however, strongly reduced by boiling with tartaric acid. Trustworthy results can, however, be obtained if the reduction is allowed to take place at the ordinary temperature, leaving the mixture for one day. Oxalic and citric acids can be employed in place of tartaric acid, but the mixture must then be boiled. With citric acid, however, the oxidation by iodine proceeds more slowly, and one hour is necessary to complete the reaction, whereas with oxalic acid, it is complete in a quarter of an hour, and with tartaric acid in 30—40 minutes. A large excess of oxalic or tartaric acid does not influence the result, but an excess of citric acid must not be employed or the results will be too high.

For each tenth of a gram of vanadic acid present in the mixture, 1 gram of the organic acid is employed. After reduction, the cold solution is mixed with potassium hydrogen carbonate in the proportion of 5 grams for each gram of organic acid employed, and then a slight excess of iodine is added. The excess of iodine is destroyed by arsenious acid, and the mixture titrated with iodine in the presence of starch.

E. C. R.

Estimation of Nitrites in Waters. By Barbet and Jandrier (*J. Pharm.*, 1896, [vi], **4**, 248—249).—The authors propose resorcinol as a substitute for metaphenylenediamine in the estimation of nitrites in water. 0·1 gram of resorcinol is dissolved in 2 c.c. of the given water, and 1 c.c. of pure concentrated sulphuric acid is added in such a way that it forms a clear layer below the aqueous solution. At the junction of the two liquids a coloration is developed, which becomes deeper after gentle shaking. At the end of an hour, the tint obtained is compared with that resulting from solutions containing known quantities of nitrite. Waters containing even $\frac{1}{10000000}$ part of nitrite give a characteristic rose coloration. J. J. S.

Apparatus for Estimating small Quantities of Marsh-Gas and other Gases in the Air of Coal-Mines. By RUDOLF JELLER (*Zeit. angw. Chem.*, 1896, 692—702).—A somewhat complicated apparatus made on the Hempel principle, but filled with water instead of mercury. The difference in pressure is noted before and after treating the gas with absorbents, or submitting it to combustion.

L. DE K.

Estimation of Invert-Sugar. By A. LEYS (*J. Pharm.*, 1896, [vi], 4, 488—490).—In the volumetric estimation of glucose and also of invert-sugar, the author finds that the final point can be observed much more readily if the saccharine solution is alkaline and not acid. It is therefore advisable, after the inversion of cane-sugar by means of hydrochloric acid, to neutralise it, or render it alkaline, with potash before titrating with Fehling's solution. J. J. S.

Conditions Affecting the Volumetric Estimation of Starch by means of a Solution of Iodine. By FANNIE T. LITTLETON (*Amer. Chem. J.*, 1897, 19, 44—49).—The author finds that, for equal weights of starch, the depth of colour produced varies with the size of the granules; moreover, the intensity of the colour produced with different quantities of starch is not proportional to the amount of starch present, and is also greatly influenced by the presence of proteid matter. The method can only be used with substances containing a large amount of starch, and the solutions to be compared should be as nearly as possible identical.

Chloroform extracts iodine from starch iodide solution, even in presence of a large excess of starch. A. H.

Different Methods for Estimating Cellulose. By H. SURINGAR and BERNHARD TOLLENS (*Zeit. angw. Chem.*, 1896, 712—719; 742—750). —The authors have made a thorough investigation of the various processes in use for the estimation of cellulose, and have tabulated the results.

Lange's process, fusing with potassium hydroxide, yields a fairly pure cellulose, but causes a considerable loss, whilst Gabriel's method of treating with glycerol and potassium hydroxide yields an impure product. The chlorine method of Cross and Bevan is only to be recommended as a conventional process for testing jute. The best process seems to be the chlorate method recommended by Schulze, but the authors have not yet made a sufficient number of experiments to be able to speak decisively. L. DE K.

Estimation of Aldehyde in Alcohol. By JOSEF PAUL (*Zeit. anal. Chem.*, 1896, 35, 647—659).—The method is a colorimetric one in which the reaction with a solution of magenta decolorised by sulphurous acid is employed, but the conditions are defined with greater precision than heretofore. To prepare the reagent, the purest 'diamond' magenta is dissolved in 1000 parts of cold water and the solution filtered; a volume which contains 0·05 gram of magenta is then mixed with an aqueous solution of sulphurous acid containing (by iodine titration) exactly 0·5 gram of H_2SO_3, and the mixture is made up to 100 c.c. In well-stoppered bottles, the reagent can be kept for

several days. The aldehyde-free alcohol required can only be obtained by boiling a large quantity (8 litres) of alcohol in a flask with an inverted condenser fed with water of 50—60°; and removing the uncondensed aldehyde vapour by inserting into the condenser a tube connected with an aspirator. After several days, the alcohol may be slowly distilled over, but the first 3 litres and the last litre must be rejected. Any form of colorimeter may be used, but those of Krüss and Duboscq are recommended as convenient. All specimens of alcohol are diluted to 30 vols. per cent. unless the amount of aldehyde present is too small to admit of such dilution. A few "type solutions" are prepared, containing 25, 50, and 100 milligrams of aldehyde per litre of (30 vols.) alcohol, and since the intensity of the colour is only proportional to the amount of aldehyde within narrow limits, it is necessary so to dilute (with pure 30 vol. alcohol) the specimen of alcohol under examination that it may contain approximately the same proportion of aldehyde as one of these type solutions before finally measuring in the colorimeter the lengths of solution which give the same depth of colour. The operation is thus performed. Equal volumes of the type solution and the alcohol to be assayed are brought to 16° by immersing them in the same vessel of water; equal volumes of the reagent are then added simultaneously, and after 25 minutes the mixtures are transferred to the colorimeter and a series of readings made as rapidly as possible. For the 25 milligram and weaker types, 1 vol. of reagent is added to 10 vols. of alcohol; for stronger types, the amount of reagent is proportionally increased. Should the observed lengths differ by more than $\frac{1}{10}$th, a fresh adjustment of aldehyde concentration is necessary, and if the adjustment of aldehyde is carried on until equal columns give equal depths of colour, the observations may be made in a pair of ordinary test-tubes of equal diameter in front of a sheet of white paper.

Acetal in alcohol may be estimated in the same way. The acetal is hydrolysed by the sulphurous acid according to the equation $C_2H_4(OC_2H_5)_2 + H_2O = C_2H_4O + 2C_2H_5 \cdot OH$, so that the acetal is calculated from the aldehyde found.

Equally good results were obtained by the use of methylviolet 5 R from the Elberfeld factory in place of magenta. M. J. S.

Action of Stannous Chloride on Ethereal Oils. By EDUARD HIRSCHSOHN (*Chem. Centr.*, 1896, i, 755; from *Pharm. Zeits. Russ.*, **35**, 65—69).—The author has found that Gurjun balsam oil and stannous chloride (Abstr., 1896, ii, 508) give a red coloration which turns violet and then blue. The behaviour of a large number of very various ethereal oils towards this reagent has now been further investigated by him; of these, only those of patchouli, musk, and valerian give a reaction similar to that of Gurjun balsam oil. The oils of celery seed, cubebs, galangal, laurel, sandal wood (some kinds), pepper, and cardamoms give a red to a pale rose colour. Wormwood and camomile oils furnish a green to bluish-green coloration. E. W. W.

General and Physical Chemistry.

Relation between the Refraction of the Elements and their Chemical Equivalents. By JOHN H. GLADSTONE (*Proc. Roy. Soc.*, 1896, **60**, 140—146).—A list of the specific refractions $(\mu - 1)/d$ and the atomic refractions $P(\mu - 1)/d$ of the elements is given, as deduced from observations of the element itself, its salts or other compounds. In a paper by the author on the refraction equivalents of the elements (*Phil. Trans.*, 1870), it was shown that if the metallic elements be arranged in the order of their specific refractions, they are roughly in the inverse order of their combining proportions. It was subsequently shown that the specific refractive energy of a metal is inversely as the square root of its combining proportion. The data collected in the present paper serve to test this generalisation throughout the whole range of the metallic elements. If S is the specific refraction and E the chemical equivalent of the metal, then $SE^{\frac{1}{2}}$ should have a constant value. For this product, the author proposes the name "refractive constant of equivalent weights." A review of the tables given shows that metals which have the same valency have the same or nearly the same constant of refraction for equivalent weights. The constants of the bivalent, trivalent, quadrivalent and apparently quinquivalent groups are practically the same, ranging about 1·01. When a metal combines in a proportion that indicates a lower valency than that ordinarily assigned to it, its constant is somewhat elevated.

If the constants are calculated for the square root of the atomic weight instead of that of the combining proportion, the following mean values are obtained :

Univalents...1·30	Trivalents.........1·75	Quinquivalents...2·19
Bivalents ...1·40	Quadrivalents ...2·12	

The fact that these numbers increase nearly in the proportion of the square roots of 2, 3, 4 and 5, indicates that the relation involved is not between the specific refraction and the atom, but rather between it and the combining proportion or chemical equivalent of the metal. This brings the optical property into analogy with Faraday's law of electro-chemical equivalents. H. C.

Influence of Temperature on Rotatory Power. By PHILIPPE A. GUYE and EMILY ASTON (*Compt. rend.*, 1897, **124**, 194—197). The authors have determined the specific rotatory powers between 15° and 100° (approximately) of valeric acid, secondary amylic alcohol, amylic benzoate, secondary amylic chloride, amylic paratoluate, propylglycol chlorobromhydrin, secondary amylic chloracetin, propylglycol chlorochloracetin, propylglycol chlorobutyrin, primary amylic alcohol, propylglycol chloracetin, propylic β-methyladipate, ethylic β-methyladipate, amylic chloracetate, methylic chlorosuccinate, ethylic chloromalate, methylic phenylglycollate, and ethylic phenylchloracetate. In all cases, the rotatory power diminishes as the temperature rises, the phenomenon being continuous throughout the interval specified. There are now at

least fifty optically active liquids the rotatory powers of which are known to diminish with a rise of temperature. C. H. B.

Rotatory Power and Structure. By PHILIPPE A. GUYE and J. GUERCHGORINE (*Compt. rend.*, 1897, **124**, 230—233).—The following specific gravities and specific rotatory powers have been determined, and the molecular refractions calculated by the n_2 formula.

	Sp. Gr. between 15° & 20°.	Mol. Refraction. (Obs.)	$[\alpha]_D$.
Amylic valerate	0·8629	49·69	+2·99
Amylic isovalerate	0·8553	50·05	+2·69
Amylic valerate (racemic)	0·8607	50·58	+3·02
Propylic valerate	0·8653	40·80	+1·99
Isopropylic valerate	0·8510	40·90	+2·54
Butylic valerate	0·8643	45·31	+1·86
Isobutylic valerate	0·8565	45·30	+1·41
Secondary butylic valerate	0·8534	45·48	+2·12
Racemic amylic valerate	0·8548	50·40	+1·42
Propylic caproate	0·8688	49·99	+1·87
Isopropylic caproate	0·8650	49·88	+2·10
Butylic caproate	0·8668	54·49	+1·61
Isobutylic caproate	0·8653	54·36	+1·28
Secondary butylic caproate	0·8656	54·10	+1·88

There are three series of isomeric propylic compounds and three series of isomeric butylic compounds amongst the ethereal salts derived from active amylic alcohol. If the gradual decrease in rotatory power in each of these series is taken into account, it follows that in all the series the propyl group behaves as if it were heavier than the isopropyl group, whilst the isobutyl group behaves as if it were heavier than the normal butyl group, and this in its turn as if it were heavier than the secondary butyl group. C. H. B.

Spectra of Metalloids in Fused Salts: Silicon. By ARNAUD DE GRAMONT (*Compt. rend.*, 1897, **124**, 192—194).—When a highly condensed spark is allowed to impinge on silicates fused on a platinum spatula (compare Abstr., 1896, ii, 585), the spectrum of the spark shows the following lines of silicon: 6969·7 strong, 6342·2 very strong, 5978·9 somewhat strong; 5960·3 distinct, 5948·0 doubtful, 5060·0 and 5045·5 very strong; 4575·7 very feeble, 4568·9 somewhat distinct, 4553·7 distinct, 4131·3 and 4129·2 somewhat strong, but diffuse. The wave-lengths are the means of determinations with the spark and the fused salts, and with a spark between silicon poles in very pure hydrogen. The most characteristic lines are 6969·7 and 6342·2 in the red, and 5060·0 and 5045·5 in the green. The latter are much more intense than the adjacent lines of platinum and air.

The spectrum is well shown by sodium silicate, and not quite so well by the potassium salt, particularly well by potassium or sodium silicofluoride, but not at all well by zinc silicate. Natural silicates, very finely powdered and fused with sodium carbonate, soon show the pairs of lines in the red and the green respectively. C. H. B.

Theory of Lead Accumulators. By C. LIEBENOFF (*Chem. Centr.*, 1896, i, 349; from *Zeit. Electrotechn. und Electrochem.*, 1896, **2**, 420—422).—According to the author's view, in secondary cells the sulphuric acid acts as the electrolyte, lead sulphate being too insoluble and water not readily dissociated. When the charging current passes into the accumulator, the ions $\overset{--}{PbO_2}$ and $\overset{++}{Pb}$ separate out, and are replaced in the solution at the expense of the lead sulphate of the plates; only when the latter has been thus fully converted into spongy lead and peroxide will separation of the ions OH and $\overset{+}{H}$ take place. During discharge, the reverse reactions take place. H. C.

Theory of Lead Accumulators. By WALTHER LOEB (*Chem. Centr.*, 1896, i, 785; from *Zeit. Electrotechn. und Electrochem.*, 1896, **2**, 495).—The author's views with reference to the reactions taking place in lead accumulators are similar to those of Liebenoff (see preceding abstract), the dissociation of the water present into H and OH ions being, however, regarded as a primary action, and essential for the production of the PbO_2 ion. H. C.

Electrical Resistivity of Pure Mercury at the Temperature of Liquid Air. By JAMES DEWAR and JOHN A. FLEMING (*Proc. Roy. Soc.*, 1896, **60**, 76—81).—The electrical resistivity of carefully purified mercury was measured between the temperature of liquid air and +35°, the results being given in the paper in tabular and curve form. The resistivity decreases gradually from +35° to the temperature −36° on the platinum scale. At this point, the resistivity rapidly decreases to about one-quarter of its value in falling from −36° to −50°, and this sudden change all takes place within the range of about 14° of temperature. At the temperature of −50° on the platinum scale, the resistivity again changes direction, and continues downwards, in such a direction as to show that if produced along the same line from the lowest temperature actually observed, −204° on the platinum scale, it would pass exactly through the absolute zero of temperature on this scale. The part of the curve which corresponds with the mercury in the liquid state is almost exactly parallel to that part of the curve which corresponds with mercury in the solid condition, although, owing to the difference in the absolute values of the resistivities at these parts, the temperature coefficients, as usually defined, are very different. In the solid condition, between the temperatures of −197·9° and −97°, the mean increase in resistivity is 93·14 C. G. S. units per degree rise of temperature on the platinum scale; between −108·4° and −57·6° the mean increase in resistivity in C. G. S. units per degree is 109·6; in the liquid condition between the temperature −35·2° and 0° the mean increase per degree is 83·2 C. G. S. units. Temperatures defined by the platinum scale do not differ by more than 0·5° from the centigrade scale down to −100°, but the temperature of boiling liquid oxygen, which on the centigrade scale is denoted by −182°, is on the platinum scale denoted by −196·7°. The temperature coefficient as usually defined is therefore 0·000884 between −35° and 0°.

The measurements afford a further confirmation of the law that the

electrical resistivity of a pure metal vanishes at the absolute zero of temperature. H. C.

Electrical Resistivity of Bismuth at the Temperature of Liquid Air. By JAMES DEWAR and JOHN A. FLEMING (*Proc. Roy. Soc.*, 1896, **60**, 72—75).—The anomalous results obtained by the authors (Abstr., 1896, ii, 5) for the resistivity of certain samples of bismuth at various temperatures down to that at which air solidifies, have led them to repeat the determinations with specially prepared pure electrolytic bismuth. The values obtained show that, in the case of pure electrolytic bismuth, there is no tendency of the resistivity curve to a minimum value. Down to the lowest temperatures reached, the resistivity continues to decrease in a perfectly regular manner, and in such a way as to show that it would be no exception, in all probability, to the ordinary law, that resistivity of pure metals vanishes at the absolute zero of temperature. With this electrolytic bismuth, the observation was confirmed that the effect of a given transverse magnetic field in increasing the resistivity of bismuth is immensely increased by cooling the bismuth to the temperature of liquid air. The effect of cooling with liquid air can be more than nullified by the field, and pressed to its limit it would appear that pure bismuth, which would in all probability be made a perfect conductor by reducing to the absolute zero of temperature, would be then converted into a non-conductor, if at the same time immersed in a magnetic field of sufficient strength. H. C.

Dielectric Constants at Low Temperatures. By RICHARD ABEGG (*Ann. Phys. Chem.*, 1897, [ii], **60**, 54—60).—Making use of the method devised by Nernst (Abstr., 1894, ii, 437), the author has determined the dielectric constants for toluene, ether, acetone, amylic and ethylic alcohols, and also for a solution of 1 vol. of water in 10 vols. of ethylic alcohol, between the temperatures $+19°$ and $-87°$. The dielectric constants in all cases increase rapidly as the temperature falls, the temperature coefficient being greater the greater the value of the constant. As there is an almost constant proportion between the dielectric constant and its temperature coefficient in all cases, a formula of the type $-dD/dT=D/190$ may be taken to express the results. This gives on integration $D=ce^{-\frac{T}{190}}$, a formula which is found to be in close accordance with the experimental results. H. C.

Electromotive Force and Partition Equilibrium. By ROBERT LUTHER (*Zeit. physikal. Chem.*, 1897, **22**, 85—92).—The author replies to Bucherer's claim for priority (Abstr., 1896, ii, 461 and 586), and states that, although the results of the latter were in print earlier than his own, yet his were read as a dissertation thesis at an earlier date. The conclusions of Bucherer are not purely thermodynamical deductions, but rest on various assumptions, as, for example, the greater solubility of electrolytes in water than in aqueous alcohol. L. M. J.

Molecular Conductivity of Rubidium and Cæsium Chlorides. By BERTRAM B. BOLTWOOD (*Zeit. physikal. Chem.*, 1897, **22**, 132—133).—According to Bredig (Abstr., 1894, ii, 226), the ion velocities of rubi-

dium and cæsium, obtained by measurement of the conductivity of the chlorides, are respectively 73·5 and 73·6 at 25°. Baur, however, obtained the values 76·5 and 79·3 from the same salts (Abstr., 1896, ii, 144). The numbers being of interest from the periodic law standpoint, the conductivities were redetermined at concentrations v = 32, 64, 128, 256, 512, and 1024, giving, after correction for the conductivity of the water, the value $\mu_\infty(RbCl) = 144·5$ and $\mu_\infty(CsCl) = 144·8$, which lead to the velocities Rb = 74·3 and Cs = 74·6.

L. M. J.

Electrolytic Solution and Separation of Carbon. By ALFRED COEHN (*Chem. Centr.*, 1896, i, 985, from *Zeit. Electrotechn. und Electrochem.*, 1896, **2**, 541).—Bartoli and Papasogli noticed that, during the electrolysis of dilute sulphuric acid with carbon electrodes, carbonic oxide and carbonic anhydride make their appearance along with oxygen at the anode. By suitable alteration in the concentration of the acid, the temperature, and the current density, the author succeeded in carrying out the electrolysis in such a manner that carbonic oxide and carbonic anhydride were almost alone produced at the anode. The gaseous mixture contained 70 per cent. CO_2, about 30 per cent. CO, and 1 per cent. O_2. At low temperatures, a distintegration of the anode takes place, and suspended particles of carbon find their way into the acid. At high temperatures, carbon dissolves in the acid, the solution being coloured from yellow to a reddish-brown. If the solution thus formed is electrolysed, using a platinum cathode, a deposit of carbon is obtained, at first as a thin, coloured film and then as a graphitic deposit. The solution reduces Fehling's solution and probably contains carbohydrates. In reversal of the above process, a cell was formed by means of a lead peroxide plate and a carbon electrode, in which, working under the conditions previously maintained, the carbon acts as the soluble electrode. This gave 1·03 volt. with an external resistance of 100 ohms and yielded a constant current until the lead peroxide plate was exhausted.

H. C.

Electrolysis of Copper Sulphate Solutions. By FRITZ FOERSTER and O. SEIDEL (*Zeit. anorg. Chem.*, 1897, **14**, 106—140).—The authors' experiments prove that the electric current is capable of converting the bivalent copper ions at the cathode in copper sulphate solutions into univalent ions, whereby cuprous sulphate is formed. The latter is tolerably stable in the presence of copper sulphate in acid solution under certain conditions, but in a neutral solution, hydrolysis takes place with the separation of cuprous oxide.

The electrolysis of copper sulphate solutions containing from 4 to 0·05 equivalents per litre, either neutral or mixed, with 0·01 to 1 equivalent of sulphuric acid, and heated at 100°, was examined. The electrolyte was stirred, and protected from air by a current of pure hydrogen. From neutral and very slightly acid solutions, less cuprous oxide, and from stronger acid solutions less copper, than the quantity corresponding with the current employed is deposited. In a solution containing 2 equivalents of copper sulphate and 0·1 or 1·0 equivalent of sulphuric acid, however, with a current density of 0·135 ampères per 100 square centimetres, hardly anything is deposited at the

cathode; from this, the authors conclude that the current has effected the conversion of copper sulphate into cuprous sulphate, which, under these conditions, is stable. The stability is determined by the number of cupric ions present, and generally increases with the concentration of the copper sulphate. In neutral solution, cuprous oxide is deposited, but a N/10 solution of sulphuric acid is sufficient in a 2N solution of copper sulphate to prevent the hydrolysis to a great extent; as the solution cools, sparkling crystals of pure copper are deposited. The same crystalline deposit of copper is obtained by dissolving cuprous oxide in an acid solution of copper sulphate. In strongly acid solutions, the number of cuprous ions remaining in solution is limited, and when the limit is reached they are converted into cupric ions and copper, which is deposited at the cathode; whence, under like conditions, but with varying current densities, almost the same quantity of cuprous ions remain in solution. That these phenomena are not produced by the re-solution of the copper deposited at the cathode is shown by the appearance of the deposit, which is highly crystalline.

The electrolysis of copper sulphate solutions at the ordinary temperature with currents varying from 0·03 to 0·0012 ampère per 100 square centimetres was examined in a similar manner. Similar results are obtained, but smaller quantities of cuprous ions remain in the solution. With a very small current density of 0·011 ampère or less, the only effect of the current is the conversion of cupric into cuprous ions. As the current density increases, fewer cuprous ions are formed.

The agitation of the electrolyte by the hydrogen current brings some of the cuprous ions to the anode, whereby they are converted by the current into cupric ions, and consequently less copper is dissolved from the anode than that corresponding with the current; this effect is more pronounced in electrolytes suitable for the formation of cuprous ions. When the electrolyte is not stirred, more than the theoretical quantity of copper is dissolved from the anode owing to spontaneous solution.

In contradiction to the result obtained by Schuster (Abstr., 1894, 318), the authors find that copper is soluble to an appreciable extent in a solution of copper sulphate from which air is excluded. Copper foil was treated for 18 to 20 hours at the ordinary temperature, and for 2 hours at 100°, with solutions of copper sulphate similar to those employed in the electrolysis, and protected from the air by a current of hydrogen. In neutral solution, a beautiful crystalline deposit of cuprous oxide is obtained, and the copper foil increases in weight; in acid solutions (N/100 H_2SO_4), a decrease in weight takes place varying from 2 to 75 milligrams per 40 square centimetres of surface. The solubility increases with the concentration of the copper sulphate. Copper is quite insoluble in normal sulphuric acid at 100°.

From the above results, the authors conclude that the electrolysis of copper sulphate solutions at 100°, and at the ordinary temperature, when a small current density is employed, takes place as follows. The anode copper forms with the contiguous cupric ions cuprous ions, and the latter, under the influence of the current, are converted into cupric ions. At the cathode, the current converts the cupric ions into cuprous ions, and the latter, as soon as a certain proportion is reached,

become unstable, and are converted into cupric ions with deposition of copper or cuprous oxide.

The formation of cuprous oxide, observed with very small current density, takes place to a greater extent with high current density when the potential difference of the bath is a little above 1 volt., which voltage is necessary for the decomposition of water. The cuprous ions then unite with the hydroxyl ions to form cuprous oxide. The deposition of powdery, red copper which takes place both from neutral and acid solutions depends on the current density alone. The deposit does not contain cuprous oxide.

The formation of the black deposit which is obtained from very dilute copper sulphate solutions under a high voltage is determined by the dilution of the copper sulphate; in N/20 copper sulphate solutions, it is formed if the solution is not stirred, but on stirring, red copper is deposited; in N/100 solutions it is formed even when the solution is stirred. It is probably a compound of copper and hydrogen similar to those prepared by Mylius and Fromm (Abstr., 1894, ii, 235) by precipitating very dilute copper solutions with a more positive metal. It oxidises easily in the air with formation of water and red copper. It is also obtained from N/100 copper nitrate; if, however, a small quantity of ammonium nitrate is added and the electrolyte stirred, red copper is deposited and hydrogen evolved; with larger quantities of ammonium nitrate, red copper alone is deposited if the solution is not stirred.

Cuprous oxide is also deposited to a slight extent at the anode, and under certain conditions a yellow, amorphous precipitate is obtained, which the authors believe to be a basic cuprous sulphate.

The errors in the results obtained when a small current is measured by the copper voltameter can be eliminated to a great extent by adding alcohol to the electrolyte (Oettel, *Chem. Zeit.*, **17**, 543 and 577); the alcohol decreases the concentration of the copper ions, and therefore the solubility of the copper in its sulphate solution. Very small currents can be measured with fair accuracy by this method, provided very small cathodes are employed whereby a high current density is obtained; with a current of 0·005 ampère, the error is about 0·5 per cent. Results of like accuracy are obtained by employing an electrolyte saturated with cuprous ions, which is obtained by electrolysing a 2N copper sulphate solution with 0·1 ampère at 100° for a few hours and then allowing it to cool.

In the electrolytic refining of copper, it is advantageous to heat the electrolyte to some extent; with the same current density, the deposit at the anode at 18° contained 2·9 per cent. Ag and 62·5 per cent. Cu, at 40° it contained 10·2 per cent. Ag, 1·4 per cent. Cu, and 86 per cent. Pb. The electrolyte can be heated to 50° without influencing the yield, but above this temperature the yield decreases.

The authors point out the bearing of the above results on the theory of lead accumulators, and maintain that the formation of lead peroxide at the anode is similar to the formation of cuprous ions as described above. E. C. R.

Is a Diaphragm known that will prevent Diffusion but not the Passage of a Current? By K. Ochs (*Chem. Centr.*, 1896, i,

289; from *Zeit. Electrotechn. und Electrochem.*, 1895, **2**, 398—402).—A diaphragm that would prevent diffusion, but would allow the passage of a current might be either—

1. A membrane not permeable by the electrolyte, but permeable by the ions; or
2. A membrane permeable by the ions, and which would absorb the electrolyte but not allow its transfusion; or
3. A membrane not permeable by either electrolyte or ions, but which allows passage of the ions when these have been deprived of their charges.

Membranes of the first class are at present unknown. Those of the second order appear to be formed by precipitation of both ions in the pores of the membrane, as, for example, in the Reynier cell (a Daniell cell in which potash replaces dilute sulphuric acid) in which copper oxide forms in the pores of the cylinder dividing the copper sulphate and potash solutions. With the continual formation of the precipitate in these cases, the resistance increases, so that any advantage obtained by the non-diffusion of the electrolyte is completely nullified. A membrane of the third order might be formed if a sufficiently thin film of mercury could be obtained, as a metal like zinc could diffuse through such a film. It does not appear, however, that such a membrane would be of any practical value. Diaphragms of the required kind for practical purposes are therefore at present unknown. H. C.

Heats of Vaporisation of Liquids at their Boiling Points. By MISS DOROTHY MARSHALL (*Phil. Mag.*, 1897, [v], **43**, 27—32).—The author has determined the heats of evaporation of the following liquids by the method described in a former paper (Abstr., 1896, ii, 349).

Normal hexane	L = 79·2	Methylic iodide	L = 45·9
Methylic alcohol	261·6	Ethylic iodide	47·6
Formic acid	120·4	Ethylic bromide	58·6
Aniline	113·9	Chloroform	58·4
		Carbon tetrachloride	46·4

Experiments were made to see whether an absolute determination of L might not be obtained by a modification of the method used, a knowledge of the average strength of the current and of the potential difference across the ends of the platinum spiral during boiling being alone necessary for this purpose. The results indicate that fairly accurate absolute measurements can be thus obtained. H. C.

Determination of the Rise of the Boiling-point in Molecular Weight Determinations. By PAUL FUCHS (*Zeit. physikal. Chem.*, 1897, **22**, 72—76).—The author describes, with the aid of diagrams, the apparatus he employs for the above purpose, and for which he claims the advantages of constancy of temperature, stability, and rapidity of working. L. M. J.

Corresponding Temperatures. By J. A. GROSHANS (*Ann. Phys. Chem.*, 1897, [ii], **60**, 169—173).—The author claims to have shown in 1849 that the boiling points of two substances on the absolute scale under any given pressure p, and under the ordinary atmospheric pres-

sure, are connected with one another by the formula $T_p/T'_p = T_{atm}/T'_{atm}$ = const.

Reference is here made to determinations by Anschütz of the boiling points of 24 different organic compounds at 12 mm. and at 760 mm. pressure, and it is shown that the above formula holds with a fair degree of accuracy when water is used as a standard of comparison in each case. H. C.

Complete Freezing Point Curves of Binary Alloys containing Silver or Copper, together with another Metal. By CHARLES T. HEYCOCK and FRANCIS H. NEVILLE (*Proc. Roy. Soc.*, 1896, **60**, 160—164).—An abstract of a paper containing the results of some experiments on the freezing points of alloys of two metals, one of the two being in each case either silver or copper. Complete freezing point curves are given in the paper for the following pairs of metals—Ag-Cu, Ag-Pb, Ag-Sn, Pb-Cu, Sn-Cu, Ag-Sb. Incomplete curves are also given showing the freezing points of dilute solutions of Bi, Au, Ni, Fe, Al in copper, and of Bi, Pt, Au, Al, and Tl in silver. From the behaviour of the more dilute solutions, the latent heat of fusion of copper was calculated as 50 cal., and that of silver as 27 cal., but both numbers can only be regarded as provisional. The eutectic alloy of silver and copper occurs exactly at the composition Ag_3Cu_2, but there is no other sign of chemical union between these metals. In the silver-lead and silver-tin curves, which have a good deal of likeness to each other, the eutectic alloy contains so little silver that the curve consists almost wholly of the branch starting from pure silver. The lead-copper curve affords an excellent example of the solidification of a system consisting of two conjugate liquids, a saturated solution of lead in copper, and a saturated solution of copper in lead; at from 17 to 65 atoms of lead per 100 of the alloy the freezing point remains constant at 954°. The copper-tin curve presents many singularities probably explained by the formation of compounds. The silver-antimony curve shows an angle at Ag_3Sb, but the eutectic point, although near Ag_3Sb_2, is not at this formula. It is worthy of note that in three cases an angular depression, and not a summit, occurs at a formula point.

H. C.

Freezing Points of Binary Mixtures. By ALBERT DAHMS (*Ann. Phys. Chem.*, 1897, [ii], **60**, 119—123).—The author gives measurements of the freezing points of mixtures of acetic acid and benzene, and of acetic acid and water. The eutectic point for mixtures of acetic acid and benzene was found to be $-8{\cdot}1°$, the mixture containing 34·8 per cent. by weight of acetic acid. The eutectic point in the case of acetic acid and water was found at $-26{\cdot}55°$, when the mixture contains 58·98 per cent. by weight of acetic acid. H. C.

Determination of the Molecular Weights of some Inorganic Substances. By HEINRICH BILTZ (*Chem. Centr.*, 1896, i, 793; from *Math. natw. Mitt. Berlin*, 1896, 57—64).—The author has continued his determinations of the vapour densities of inorganic substances at very high temperatures (Abstr., 1896, ii, 152). The results previously obtained with arsenious anhydride were confirmed by a new set

of determinations. Selenium and tellurium at 1750—1800° have densities which accord with the molecular formulæ Se_2 and Te_2. The same formulæ were obtained by Troost and Deville at 1000° by the Dumas method, but an examination of the results of these investigators has led the author to the conclusion that they are untrustworthy. H. C.

Racemism and the Heat Changes Produced when Liquids are Mixed. II. By ALBERT LADENBURG (*Ber.*, 1897, **30**, 485—486. Compare Abstr., 1895, ii, 485).—When coniine is mixed with a liquid of the same specific gravity, which does not react chemically with it and does not cause contraction or expansion, no fall of temperature is observed. Thus when equal volumes of coniine and a mixture of piperidine and di-isobutylamine are brought together at 17°, a rise of 0·19° occurs, the specific gravity of the mixture being practically the same as that of its constituents. This confirms the view previously put forward by the author, that the fall of temperature observed when dextro-coniine and lævo-coniine are mixed is due to the formation of a racemic compound. A. H.

Spontaneous Change of Oxygen into Ozone, and a Remarkable Type of Dissociation. By WILLIAM SUTHERLAND (*Phil. Mag.*, 1897 [v], **43**, 201—214).—Bohr has placed on record a singular discontinuity in the behaviour of rarefied oxygen under a pressure of 0·7 mm., as well as a pronounced departure from Boyle's law, and Crookes, in his study of radiometer repulsion for different gases, found that oxygen at a pressure of about 0·76 mm. shows a remarkable difference from other gases, and the anomaly continues until a pressure of about $300/10^6$ to $200/10^6$ atm. is reached. The author finds that a process of association or combination of the O_2 molecules to form O_3, that is ozone, explains one of Bohr's equations and the cessation of anomaly in Crookes's experiments. It is therefore necessary in compressing pure O_3 that a pressure should be reached at which the O_3 begins to dissociate into O_2, and progressive increase of pressure produces progressive dissociation of O_3 into O_2. It appears that there is a certain periodic collision with one another which the O_3 molecules cannot stand, and this implies that the period is identical with some natural period of vibration in the molecule. This singular instance of dissociation is applied to explain the anomalous expansion of rarefied oxygen observed by Baly and Ramsay (Abstr., 1895, ii, 38), and it is pointed out that it would indicate the presence of ozone in quantity in the higher regions of the atmosphere. H. C.

Dissociation of Chlorine Hydrate in Aqueous Solution at 0°. By ALEXANDER A. JAKOWKIN (*Ber.*, 1897, **30**, 518—521).—The dissociation of chlorine in very dilute solutions is represented by the equation $Cl_2,Aq \rightleftarrows (HCl + HClO)Aq$, since the electrical conductivity of such solutions at 0° is equal to that of hydrochloric acid solutions containing the same amount of hydrogen chloride. According to the author, hypochlorous acid is no electrolyte. In more concentrated solutions, the conductivity of chlorine is much less.

The dissociation of bromine hydrate at 0° is extremely small, and

can only be observed in very dilute solutions. Since the dissociation of both chlorine and bromine takes place with absorption of heat, it follows that the amount of dissociation increases with the temperature. All the cases of equilibrium studied, some 150 in number, are in complete accord with the theory of electrolytic dissociation according to the equation $Cl_2,Aq = (\bar{Cl} + \overset{+}{H} + HClO)Aq$. This was proved by calculating the isotherms required by the above equation when the chlorine is divided between water and carbon tetrachloride (the latter absorbs neither hydrochloric nor hypochlorous acid from aqueous solutions).

An addition of 0·5—0·1 normal hydrochloric acid completely prevents the formation of chlorine hydrate. An addition of normal or bisnormal acid, however, induces a stronger absorption of chlorine on account of the formation of HCl_3. J. J. S.

Apparatus for the Rapid Determination of the Surface Tension of Liquids. By CHARLES E. LINEBARGER (*Amer. J. Sci.*, 1896, [iv], 2, 108—122, and *J. Amer. Chem. Soc.*, 1896, 18, 514—532).—Jaeger (*Wien. Akad. Ber.*, 1891, 245) has described a method for determining the surface tension of liquids by employing two capillary tubes of different bores and measuring the difference of the depths to which they were plunged in a liquid when air forced out of them was at the same pressure. The author describes an apparatus which is a modification of the one used by Jaeger for effecting determinations in this manner. The equation which Jaeger gives for the calculation of the results appears to be merely approximate, and does not stand a severe scrutiny; a simple empirical relation was discovered, however, which brings the determinations of surface tensions by this method into agreement with those of Ramsay and Shields. This relation is $\gamma = chs + s^2$, where γ represents the capillary constant in dynes per centimetre, c the "apparatus constant," h the distance between the ends of the tubes, and s the specific gravity. This formula was found to stand the test of comparison with ten liquids of different properties when two sets of tubes were employed, but it is not claimed that it will furnish accurate results for any liquid whatsover, as the "apparatus constant" may differ with different liquids. H. C.

Surface Tension of Mixtures of Normal Liquids. By CHARLES E. LINEBARGER (*Amer. J. Sci.*, 1896, [iv], 2, 226—228).—With the apparatus described in a previous communication (preceding abstract) the author has measured the surface tensions of mixtures of some normal liquids. Solutions of toluene and ether in benzene, of turpentine, carbon bisulphide, and ethylic benzoate in toluene, and of ethylic iodide and carbon bisulphide in ether were taken. In the majority of cases, the surface tensions of normal liquids are not calculable by the rule of mixtures from the surface tensions of the pure liquids. If the observed value is greater or less than the calculated value for any one mixture of two liquids, it is also greater or less for any other mixture of the same two liquids. H. C.

Some Thoughts about Liquids. By CLARENCE L. SPEYERS (*J. Amer. Chem. Soc.*, 1896, 18, 724—737).—The boundary dividing

vapour from liquid is commonly supposed to be at the surface of the liquid, although the possibility of a differentiation occurring inside the liquid does not seem to be denied. The tendency for a liquid to vaporise, and the pressure of its saturated vapour, is evidently a function of temperature only. There seems to be no reason, therefore, why the fluid should not separate into vapour and liquid within the surface of the liquid.

Suppose n molecules of a substance which does not dissociate on dissolving, say sugar, are dissolved in water. Let ν be the number of molecules of dissolved vapour after the n molecules of substance have been dissolved, then the total number of molecules present in solution will be $\nu+n$, and the relative number of molecules of substance dissolved to the total number of molecules in solution is $n/(\nu+n)$. Let j be the concentration of the dissolved vapour when alone in the liquid, and j' its concentration after the new substance has been added. Since the molecule of every substance occupies the same volume, the decrease in concentration $j-j'$ will be the same whatever the substance dissolved may be, or the decrease in concentration of the dissolved vapour is proportional to the number of molecules dissolved in a certain fixed volume of solution. If the temperature be constant, the concentration of the dissolved water vapour cannot rise above the value j, hence the number of molecules in unit volume must be fixed, that is $\nu+n=$constant. We have therefore $(j-j')j=a.n/(\nu+n)$, where a is a constant, $j-j'$ can be calculated by van't Hoff's law, and n is known, but the other quantities are not, so neither j nor ν can be calculated from this equation.

The concentration of the dissolved vapour is, however, measured by its osmotic pressure. Let π and p be the osmotic pressures of the dissolved vapour and of the vapour pressure of the pure solvent respectively, and π' and p' be the corresponding quantities when a substance is in solution. Then by means of a thermodynamic cycle it may be shown that $\pi/\pi'=(p/p')x$, where x denotes the number of molecules of gaseous vapour necessary to make one molecule of dissolved vapour, a quantity which the author assumes to be equal to 1. Since $j/j'=\pi/\pi'$, we have $(p-p')/p=a.n/(\nu+n)$. But this will also be equal to $n/(N+n)$, where N is the number of molecules of liquid in which n molecules of substance have been dissolved, for by experiment $(p-p')/p=n(N+n)$. If the value of n is so small that it may be neglected in comparison with ν and N, we get $a.n/\nu=n/N$, or $a=n/N$. From this we have

$$\frac{\nu}{N}\,\frac{n}{\nu+n}=\frac{n}{N+n}\quad\text{or}\quad \nu=N,$$

that is, the concentration of the dissolved vapour is the same as the concentration of the liquid, or in other words, all the solvent is to be considered as dissolved vapour. This is, in effect, the same conclusion that van der Waals reached by a very different method in his celebrated treatise.

A liquid is to be looked on, then, as a condensed gas, not simply condensed in the sense that it is matter compressed into smaller space, but condensed in the sense that the gaseous activity, pressure, is carried into the liquid condition, and we are to treat a liquid as

we would a gas. A substance dissolved is simply brought into the same condition that the liquid is in, and consequently should have the same property of exerting an osmotic pressure that the liquid has.

H. C.

Determination of the Diffusion Coefficients of some Gases in Water. By C. GUSTAV HÜFNER (*Ann. Phys. Chem.*, 1897, [ii], **60**, 134—168).—The author draws attention to the fact that, since Stefan showed in 1878 that Fick's law of diffusion holds in the case of carbonic anhydride in water or alcohol, no determinations of the rates of diffusion of gases in liquids have been made, with the exception of Müller's experiments on ammonia in water and alcohol (Abstr., 1891, 1147). Experimental difficulties account in some measure for this fact, since, if the gas is placed above the liquid, as it dissolves the liquid becomes heavier and sinks, and so produces currents which disturb the regular course of the diffusion, a difficulty only to be avoided by the use of tubes of very small bore. In order to place the liquid above the gas and so prevent the formation of concentration currents, the author uses a tube divided into two portions by means of a thin plug of hydrophane, placing water in the upper portion of this tube, and then allowing the gas to diffuse through the hydrophane into the water. Taking the day as unit of time and the centimetre as unit of length, if k is the coefficient of diffusion, $k = vl/a$, where v is the volume of gas measured at 0° and 760 mm. that will diffuse under a pressure of 1 atm. through a column of water 1 cm. in length and 1 cm.^{2} in area, and a is the coefficient of absorption of the gas. Exner has shown that the interchanging volumes of two gases, separated from one another by a soap film, are proportional to their coefficients of absorption and inversely proportional to the square roots of their densities. With the aid of Stefan's value for the diffusion coefficient of carbonic anhydride in water and the known densities of the different gases, it is possible therefore to calculate the coefficients of diffusion for gases, as these should be inversely proportional to the square roots of their densities. In the following table are given the numbers thus calculated and the numbers obtained for the temperature 16°, taking Stefan's value for k in the case of carbonic anhydride at 1·38, and using this as the basis in the calculations.

	$k_{\text{cal.}}$	$k_{\text{obs.}}$
Carbonic anhydride	(1·38)	1·37
Hydrogen	6·47	4·09, 4·45, 7·53
Oxygen	1·62	1·62
Nitrogen	1·73	1·73
Nitrous oxide	1·34	1·35
Chlorine	1·087	1·098

The agreement obtained in the above cases is not found when the value of k for ammonia is taken from Müller's experiments, as in this case the calculated value for k is 2·22 and the observed value is found to be 15·96.

H. C.

Attempt to Determine the Adiabatic Relations of Ethylic Oxide. By EDGAR P. PERMAN, WILLIAM RAMSAY, and J. ROSE-INNES (*Proc. Roy. Soc.*, 1896, **60**, 336—337).—The wave-length of sound in

gaseous and in liquid ethylic oxide was determined by the Kundt method, between limits of temperature ranging from 100° to 200°, and of pressure ranging from 4000 mm. to 31,000 mm. of mercury, and of volume ranging from 2·6 c.c. per gram to 71 c.c. per gram. Ramsay and Young showed that for ether (and some other liquids) a linear relation subsists between pressure and temperature, volume being kept constant, so that $p = bT - a$. It has been found that a similar relation obtains between adiabatic elasticity and temperature, volume, as before, being kept constant; so that, within limits of experimental error, if E stands for adiabatic elasticity, $E = gT - h$, where g and h are functions of the volume only. Between these two equations, we may eliminate T, and so express E as a linear function of p, volume being kept constant. The coefficient of p in such an equation would be g/b, and this fraction, on being calculated from the data available, proves to be nearly constant. If g/b is treated as strictly constant, it is possible to integrate the resulting differential equation, and from the complete primitive to draw a set of adiabatic curves, this being the first time that adiabatic curves have been obtained for any substance except perfect gases. H. C.

Solubility of Hydrated Mixed Crystals. By WILLEM STORTENBEKER (*Zeit. physikal. Chem.*, 1897, **22**, 60—71).—The crystallisation of solutions containing zinc and copper sulphates was investigated in the endeavour to obtain experimental proofs of the views published in the author's previous paper (Abstr., 1896, ii, 13). The results obtained were: (1) Solutions containing 21·5—100 per cent. mols. of copper sulphate crystallise in triclinic crystals with but little zinc, yielding by recrystallisation almost pure copper sulphate. (2) Solutions of 8·4—21·5 per cent. mols. of copper sulphate gave monoclinic pseudo-rhombohedra with $7H_2O$, the composition of which differs but slightly from that of the solution. (3) Solutions of 0—8·4 per cent. mols. of copper sulphate give rhombic crystals with little copper, yielding by re-crystallisation almost pure zinc sulphate. These results are expressed in the accompanying table, together with Retgers' values, the number giving the percentage of copper sulphate.

	Rhombic.	Monoclinic.	Triclinic.
Solutions	0—8·36	8·36—21·5	21·5—100
Crystals	0—1·97	14·9 —31·9	82·9—100
Crystals (Retgers)	0—2·34	16·8 —34·6	92·1—100

The solubility isothermal, therefore, consists of three portions, and examples were obtained of each of the labile states, crystals being obtained having the composition represented by each portion of the curve. L. M. J.

Solid Solutions. By GIACOMO L. CIAMICIAN and FELICE GARELLI (*Zeit. physikal. Chem.*, 1897, **22**, 134—135).—With respect to Bodländer's deductions from their work (this vol., ii, 133), the authors point out that his conclusions regarding the formation of a solid solution of salicylic

and benzoic acids had been anticipated by them, and further, the correct method of determining the partition ratio had been employed by them in their paper. L. M. J.

Constitution of Salt Solutions. By HEINRICH LEY (*Zeit. physikal. Chem.*, 1897, **22**, 77—84).—The colour of a solution of cupric chloride changes from blue to green when the solution is heated, the temperature at which the change occurs increasing with the concentration, and according to the hydrate theory this change is due to the passage from the hydrate $CuCl_2,3H_2O$ to $CuCl_2,2H_2O$. The latter salt, however, is not green, but blue, the ordinary green colour being due to a superficially condensed solution, and the author regards the colour change as due to a change in the degree of dissociation of the compound. Measurements of the electrical conductivity at temperatures varying from 18·7° to 80° showed the increase to be perfectly regular with no breaks in the curve, and the value $d\lambda/dT$ to decrease from 0·9 to 0·66. In solvents other than water, the colour varies, being green in alcohol, yellowish-green in acetone, yellow in urethane, and blue in pyridine. The determination of the molecular weight in these solutions gave values, 133—136 in alcohol, and 164—194 in acetone, the conductivity being $\lambda_{16} = 2·16$ and 6·1, whilst in pyridine $\lambda_{30} = 0·05$, so that the blue colour of the pyridine solution is not due to copper ions, but to an undecomposed cupric chloride-pyridine compound. L. M. J.

Isomorphous Mixtures. By HERMANN AMBRONN and MAX LE BLANC (*Zeit. physikal. Chem.*, 1897, 121—131).—A controversial paper in which the authors uphold their views against those of Küster (Abstr., 1895, ii, 257), regarding isomorphous mixtures as mixtures in which no molecular interpenetration occurs. L. M. J.

False Equilibria of Hydrogen Selenide. By H. PÉLABON (*Compt. rend.*, 1897, **124**, 360—363).—The author has determined the respective limits of direct formation and of decomposition of hydrogen selenide when the substances are maintained at given temperatures for comparatively long periods, such as 20 or 40 days. The lowest temperature at which any direct formation of hydrogen selenide was observed is 250°. The results are represented by two curves, and the area between them corresponds with Duhem's "region of false equilibria." The two curves are further apart the lower the temperature, and they are each further from the curve of true equilibria the lower the temperature. Both, however, merge into the curve of true equilibria at temperatures which approximate to 320°. Above 325°, the limits of formation and decomposition coincide. C. H. B.

Third Annual Report of Committee on Atomic Weights. By FRANK W. CLARKE (*J. Amer. Chem. Soc.*, 1896, **18**, 197—214).—A summary of atomic weight determinations published during 1895, with a complete *table of atomic weights recalculated from all available data.* H. C.

A New Form of Vacuum Pump. By J. WETZEL (*Ber.*, 1897, **30**, 537—538).—In this pump, a drawing of which is given in the paper, a bulb having a narrow outlet is blown on the tube imme-

diately under the injector; by this means, the effective action of the pump is doubled, whilst less water is used than in the ordinary form. Since, also, the time occupied in exhaustion is shorter, this pump is especially adapted for distillation under diminished pressure.

J. F. T.

Inorganic Chemistry.

Decomposition and Formation of Hydrogen Iodide. By MAX BODENSTEIN (*Zeit. physikal. Chem.*, 1897, **22**, 1—22).—The author's previous experiments on this subject (Abstr., 1893, ii, 369; 1894, ii, 12) were not in complete accord with theoretical deductions, and they were therefore repeated with very great experimental precautions. It was found that when hydrogen and iodine combine, the quantity of hydrogen iodide found by titration with sodium hydroxide did not correspond with that calculated from the loss of hydrogen and iodine, whilst the difference between the two values was almost independent of the quantity of gases employed and of the duration of the experiment. This, the author considers, is due to the combination of the iodide with the alkali of the glass, and experiments indicated an approximate proportionality between the surface area of the glass and the loss of iodide. In the experiments, this must be allowed for, and when the correction is made, the apparent increase of decomposition with pressure (Abstr., 1894, ii, 12) is not found to exist. The mean values for the amounts of iodide decomposed at the boiling points of sulphur and mercury were found to be 0·2198 and 0·1946, the corresponding values for the equilibrium constant, $K = C_I C_H / C^2_{HI}$, being 0·0212 and 0·0176; the individual results, however, varied considerably. The velocity constant, as calculated for the bimolecular reaction $2HI \leftrightarrows H_2 + I_2$, gave the following values.

	½ atm.	1 atm.	1½ atm.	2 atm.
Sulphur vapour	0·00278	0·00563	0·00867	0·01223
Mercury vapour	0·0000362	0·0000748	0·0001221	0·0001647

The values are approximately proportional to the pressure, and this obtains theoretically in the case of bimolecular reactions. Other experiments were initiated to test whether a minimum decomposition exists at 320°, as indicated by the earlier experiments (*loc. cit.*), but the results are not yet available. L. M. J.

Decomposition of Hydrogen Iodide by Light. By MAX BODENSTEIN (*Zeit. physikal. Chem.*, 1897, **22**, 23—33).—The author has investigated the decomposition of hydrogen iodide by light, and finds that the equation, $dx/dm = k\ (1 - x)$, leads to an approximately constant value for k (m = light intensity x time). The reaction is therefore unimolecular, not bimolecular, and is represented by the equation

HI = H + I, and differs, therefore, from the decomposition induced by high temperatures (preceding abstract). Hence the action of light, in the author's opinion, does not render the whole volume of gas more capable of decomposition, but each light ray of the necessary intensity decomposes into its elements the molecules of hydrogen iodide in its path. L. M. J.

Atmospheric Ozone on Mount Blanc. By MAURICE DE THIERRY (*Compt. rend.*, 1897, **124**, 460—463).—In August, 1896, the air at Chamounix at a height of 1050 metres was found to contain 3·5 to 3·9 milligrams of ozone in 100 cubic metres of air. At the Grands Mulets, at a height of 3020 metres, the quantity found 10 days later was 9·4 milligrams in 100 cubic metres. These numbers are much higher than the quantities found at Mountsouris (1·9 to 4·0), and it seems clear that the proportion of ozone increases with the altitude. The estimations were made by passing the air through a standard solution of sodium arsenite containing potassium iodide free from iodate.

C. H. B.

Production of Active Oxygen by the Slow Oxidation of Triethylphosphine and of Benzaldehyde. By W. P. JORISSEN (*Zeit. physikal. Chem.*, 1897, **22**, 34—53).—During the slow oxidation of many substances in air or oxygen, a portion of the oxygen is changed into an active modification. In the case of phosphorus, 2 atoms of phosphorus renders active 1 atom of oxygen (Abstr., 1895, ii, 212 and 262), and the author's experiments were conducted with the object of determining the corresponding ratio in the case of triethylphosphine and of benzaldehyde. The first compound was found, by oxidation in air, to require more oxygen than that theoretically necessary for conversion into triethylphosphine oxide, and this was found to be due to the formation of small quantities of ethylic diethylhypophosphite. The results were no simpler when air at low pressure was employed, but in the presence of excess of water, the oxidation was found to proceed in such a manner as to produce nothing but the phosphine oxide. The active oxygen was determined by the use of commercial sodium indigosulphonate, and numerous experiments proved that the quantity is equal to that required for the oxidation.

Benzaldehyde, by slow oxidation, passes completely into benzoic acid, the action being greatly accelerated by light, although it proceeds also in darkness. In this case also, the quantity of oxygen required for oxidation is equal to that rendered active. Analogous results, in the case of the oxidation of metals, had been previously obtained by Schönbein, Träube (Abstr., 1893, ii, 412), and Bodländer. The opinions of various chemists on this action are reviewed, and the author considers his own results to be in complete agreement with the views expressed by Van't Hoff (Abstr., 1895, ii, 262). L. M. J.

So-called 'Autoxidation.' By RUDOLF IHLE (*Zeit. physikal. Chem.*, 1897, **22**, 114—120).—The oxidising power of water containing dissolved air is greatly affected by the dissolution in it of various salts; thus, in solutions of hydroxides, carbonates, phosphates, borates, and nitrites, metals remain bright for a considerable period, although they

rapidly tarnish in pure water or solutions of chlorides, bromides, iodides, nitrates, &c. The author considers the oxidation to be due to the union of the metallic ions with negative hydroxyl ions resulting in the formation of a hydroxide, the ionisation of more metal and production of more hydroxyl by the dissolved oxygen. The accelerative influence of the neutral salts is a catalytic action similar to their effect on sugar inversion. The potential of the oxygen, and hence its tendency to form hydroxyl ions, is dependent on the concentration of these already present in the liquid, and is therefore diminished by the dissolution of salts which yield OH ions. The course of the reaction may probably be represented thus: $M'' + 2OH{\cdot}H = M(OH)_2 + H_2$; $H_2 + O_2 = H_2O_2$; $M + H_2O_2 = M(OH)_2$. This view is supported by the fact that the addition of hydrogen peroxide acts similarly to air or oxygen. Owing to the peculiar dissociation of hydrogen peroxide, it acts as an oxidising or a reducing agent. Thus in acid solution its potential (against bright platinum) is $-1{\cdot}078$, and in alkaline solution $-0{\cdot}367$, and hence substances whose potentials lie between these limits would be oxidised in acid solution and reduced in alkaline, examples of such actions being given. L. M. J.

Pyrosulphuryl Chloride. By J. ADOLPHE BESSON (*Compt. rend.*, 1897, **124**, 401—403).—Pyrosulphuryl chloride partially decomposes when boiled under ordinary pressure, but it can be fractionated under reduced pressure, and boils at 53° under a pressure of 15 mm., whilst sulphuric monochlorhydrin boils at 65° under the same pressure. It can be freed from chlorine by agitation with mercury, care being taken to keep the temperature well below 60°. Sulphuric anhydride and sulphuric monochlorhydrin are removed by adding phosphorus pentachloride in excess, and the pyrosulphuryl chloride is then readily purified by fractionation. When pure, it boils at 142—143° under a pressure of 765 mm., and when strongly cooled forms a white, crystalline solid which melts at $-39°$. Pure sulphuric monochlorhydrin boils at 152° under a pressure of 765 mm., and does not solidify at $-75°$.

Attempts to obtain pyrosulphuryl chloride by heating sulphuryl chloride and sulphuric anhydride at 100°, or by subjecting them to prolonged exposure to sunlight, were unsuccessful. Dry hydrogen bromide acts on the chloride at 50° with liberation of sulphurous anhydride and bromine and formation of sulphuric monochlorhydrin, the latter being in its turn completely decomposed by prolonged action of the hydrogen bromide, $2SO_2(OH)Cl + 2HBr = Br_2 + 2HCl + SO_2 + H_2SO_4$. Hydrogen iodide acts on the chloride cooled in a mixture of ice and salt, the products being the same as with hydrogen bromide, together with some hydrogen sulphide and sulphur. Hydrogen sulphide acts slowly on pyrosulphuryl chloride in the cold, the principal reaction being $S_2O_5Cl_2 + H_2S = S + 2HCl + SO_3 + SO_2$; on heating the reaction, $3S_2O_5Cl_2 + 2H_2S = S_2Cl_2 + HCl + 3SO_2 + 3SO_2(OH)Cl$, which is secondary in the cold, becomes the chief or even the only reaction. Dry hydrogen phosphide also decomposes the chloride at the ordinary temperature, metaphosphoric acid and the sulphide P_4S_3 being amongst the products. C. H. B.

Action of Dilute Nitric Acid on Nitrates in Presence of Ether. By CHARLES TANRET (*Compt. rend.*, 1897, 124, 463—466).—When water containing nitric acid is agitated with aqueous ether, the acid is divided between the water and the ether in a constant ratio which is independent of the relative volumes of the two liquids, but varies with the temperature and concentration. The following coefficients were observed.

Nitric acid in 100	0·25	0·50	1·0	2·0	10·0	18—40	45
Coefficient of division...	1 : 160	1 : 100	1 : 66	1 : 42	1 : 17	1 : 12 to 1 : 10	1 : 8·5

In presence of soluble nitrates, these coefficients are much higher, and increase with increasing quantities of a given nitrate, but vary also with equal quantities of different nitrates. With 5 grams of dry nitrate dissolved in 20 c.c. of nitric acid of 1 : 100, the coefficients vary in a noteworthy manner. For metals of the same or neighbouring families, the coefficients fall as the atomic weights rise, whilst at the same time they are inversely proportional to the weight of the metal contained in the nitrates. If, however, the coefficients are considered with respect to the weight of the radicle NO_3 contained in the nitrates, curious geometric progressions are observed with the alkali metals, the metals of the alkali earths, lead and thallium, and zinc and cadmium.

The effect of the nitrates may be due to two causes. Acid nitrates may be formed, the dissociation of which may be limited by the increasing quantity of normal salt added, these acid nitrates being afterwards dissociated by the ether, which takes up part of the acid. When large quantities of nitrates are added, they may form hydrates with part of the water, and thus increase the concentration of the acid and thereby raise the coefficient. C. H. B.

Nitrogen Sulphide. By WILHELM MUTHMANN and E. SEITTER (*Ber.*, 1897, 30, 627—631. Compare Abstr., 1896, ii, 298).—The *tetrachloride* of nitrogen sulphide, $N_4S_4Cl_4$, was first obtained by Demarçay (Abstr., 1881, 346) on suspending nitrogen sulphide in chloroform and passing dry chlorine through the liquid; it is excessively unstable, and when exposed to moist air, rapidly becomes converted into a black, tarry mass.

Thiotrithiazyl chloride, N_3S_4Cl, is obtained from nitrogen sulphide by the action of warm sulphur dichloride diluted with chloroform; it is more conveniently prepared by heating nitrogen sulphide with acetic chloride (4 parts) in a reflux apparatus for half an hour, when it is obtained as an intensely yellow, crystalline powder, exhibiting the properties attributed to it by Demarçay. On boiling the substance with alcohol during a short period, and treating the liquid with a few drops of alcoholic potash, an intense, violet-red coloration is developed, and does not immediately disappear on dilution with water. Ammonia gas is rapidly absorbed by the dry compound, which explodes violently after a few minutes; if thiotrithiazyl chloride is suspended in chloroform and submitted to the action of the gas, the liquid becomes orange-red, and ammonium chloride and sulphide are produced, nitrogen sulphide being regenerated.

Thiotrithiazyl nitrate, $N_3S_4NO_3$, is produced on dissolving the chloride in highly concentrated nitric acid and evaporating the yellow liquid

in a vacuum; the substance, which is very explosive, crystallises in beautiful, sulphur-yellow, transparent prisms 1 cm. in length, and when preserved during some days becomes opaque and acquires the odour of sulphurous anhydride and oxides of nitrogen. The solution in water is yellow and transparent, but becomes opaque in a few minutes, depositing a black substance mixed with much sulphur; a red liquid is obtained on boiling the compound with alcohol.

Thiotrithiazyl bromide, N_3S_4Br, obtained by dissolving nitrogen sulphide and sulphur dibromide (5 parts) in carbon bisulphide, crystallises in small, yellow needles; it is also formed when excess of bromine acts on thiotrithiazyl chloride in warm carbon bisulphide, and is identical with the compound produced on exposing the tetrabromide of nitrogen sulphide to the action of moist air (compare Clever and Muthmann, *loc. cit.*). The substance is stable in air, and when water is boiled with it, ammonium bromide, sulphur, and sulphurous anhydride are produced; hot dilute alkalis give rise to ammonia, along with alkali bromide, thiosulphate, and sulphide.

Thiotrithiazyl iodide, N_3S_4I, is prepared by dissolving thiotrithiazyl chloride in ice cold water and immediately adding excess of an ice cold solution of potassium iodide; it is a dark red, crystalline powder which decomposes spontaneously on exposure to the air, vapours of iodine being evolved. The compound is also obtained by acting on the chloride with iodine dissolved in methylic alcohol, but it invariably contains chlorine when prepared in this way.

Thiotrithiazyl thiocyanate, N_3S_4CNS, is obtained by adding a solution of potassium thiocyanate to an ice cold solution of thiotrithiazyl chloride or nitrate; it crystallises in lustrous, bronze leaflets and resists the action of air. The salt dissolves somewhat readily in benzene and chloroform.

The authors regard these compounds as containing a radicle composed of sulphur and nitrogen, and having the formula N_3S_4; from this point of view, the salts have the constitutional formula

$$S_2{<}\begin{matrix}N\cdot S\\N\cdot S\end{matrix}{>}N\cdot X.$$

M. O. F.

Metaphosphoric Acid. By MARCELLIN P. E. BERTHELOT and GUSTAVE ANDRÉ (*Compt. rend.*, 1897, **124**, 265—269).—Metaphosphoric acid, when dissolved in water, changes mainly into orthophosphoric acid, the quantity of pyrophosphoric acid that is formed being always very small. Sodium metaphosphate in aqueous solution gradually becomes acid owing to its conversion into orthophosphate and pyrophosphate. Metaphosphate that has been prepared at 280° changes somewhat rapidly, but that prepared at a high temperature alters very slowly at the ordinary temperature, provided neither acid nor alkali is present. In the case of the former, about 45 per cent. is converted into the ortho-salt in the act of dissolution, and afterwards the change is more gradual. Metaphosphoric acid, prepared by the dehydration of the ortho-acid, behaves similarly when dissolved in water; the change is at first rapid and afterwards becomes more gradual, but the rate of change increases with the concentration of the solution.

In any case, the method described (this vol., ii, 283) for the estima-

tion of pyrophosphoric acid is not applicable to its separation from metaphosphoric acid, because the latter yields the same precipitate when treated in the same way. C. H. B.

Sulphoxyarsenates [Thioarsenates]. By R. F. WEINLAND and O. RUMPF (*Zeit. anorg. Chem.*, 1897, **14**, 42—65. See also Abstr., 1896, ii, 473).—Sodium monothioarsenate, $Na_3AsSO_3,12H_2O$, prepared by the method previously described, crystallises in colourless, transparent crystals belonging to the rhombic system

$$[a : b : c = 0\cdot9199 : 1 : 0\cdot6602].$$

This salt is also obtained together with the dithioarsenate by boiling an aqueous solution of sodium arsenite with sodium polysulphide, and also by boiling sodium arsenite with sodium monosulphide; in the latter case, however, the dithioarsenate and tetrathioarsenate Na_3AsS_4 are also formed. The mixed salts, which have a composition similar to Geuther's sodium trisulphoxydiarsenate and to Preis's sodium pentasulphoxytetrarsenate, are separated by fractional precipitation with alcohol.

The formation of sodium monothioarsenate from sodium arsenite and sulphur, and the gradual decomposition of free monothioarsenic acid into arsenious acid and sulphur, is very similar to the formation of sodium thiosulphate and the decomposition of thiosulphuric acid. On the other hand, the authors were unable to obtain sodium monothioarsenate by the action of iodine on a mixture of sodium arsenite and sodium monosulphide, neither were they able to obtain a compound similar to sodium tetrathionate by the action of iodine on sodium monothioarsenate. It is probable, therefore, that monothioarsenic acid contains 3 hydroxyl groups, the sulphur being united to the arsenic atom by both bonds. Sodium monothioarsenate gradually effloresces on exposure to the air; it may be boiled in aqueous solution without decomposition, but when the solution is heated in a sealed tube at 150°, it yields sodium arsenate and sodium tetrathioarsenate. If boiled with concentrated sodium hydroxide, it undergoes but very slight decomposition, although the mixture, if evaporated to dryness, yields sodium sulphide, sodium arsenate, and much undecomposed monothioarsenate. It is also stable towards sodium hydrogen sulphide and sodium sulphide, but when boiled with sodium bisulphide it is converted into sodium dithioarsenate and arsenate. A boiling, concentrated, aqueous solution of the salt dissolves a small quantity of sulphur, which, however, separates completely as the solution cools.

Sodium monoselenoarsenate, $Na_3AsSeO_3 + 12H_2O$, prepared in a manner similar to the preceding salt, crystallises in colourless, transparent, rhombic crystals which are isomorphous with the preceding salt $[a : b : c = 0\cdot9284 : 1 : 0\cdot6409]$. When pure, it is fairly stable on exposure to air, but gradually becomes covered with a red skin of selenium; exposure to direct sunlight completely decomposes it. In aqueous solution, it is partially decomposed into selenium and arsenious acid at the ordinary temperature, more quickly on heating; a complete and immediate decomposition takes place on the addition of hydrochloric acid.

The corresponding tellurium compound was not obtained pure, as the product is decomposed by water with separation of tellurium.

Potassium monothioarsenate, $K_3AsSO_3 + 2H_2O$, is obtained in a crude state in a similar manner to the sodium salt, but the pure salt is most conveniently prepared by dissolving potassium dihydrogen monothioarsenate in concentrated potassium hydroxide free from carbonate, and allowing the mixture to crystallise by spontaneously evaporating over sulphuric acid and potassium hydroxide; it crystallises in colourless prisms. The *ammonium* salt $(NH_4)_3AsSO_3 + 3H_2O$, which is obtained together with the arsenate and tetrathioarsenate, is separated by fractional precipitation with alcoholic ammonia; it crystallises in small, lustrous leaflets. The *barium* salt crystallises with $6H_2O$; it is prepared by precipitating a solution of the sodium salt with barium chloride. The *sodium barium* salt, $NaBaAsSO_3 + 9H_2O$, is obtained by adding barium chloride to a solution of the sodium salt until a permanent precipitate ceases to be formed; it crystallises in small, colourless cubes or hollow, four-sided pyramids. The corresponding *sodium barium monoselenoarsenate,* obtained in a similar way, crystallises in four-sided prisms.

Monosodium monothioarsenate, NaH_2AsSO_3, obtained as previously described by the action of salicylic acid (2 mols.) on the trisodium salt, crystallises in microscopic, colourless prisms; it reddens litmus, decomposes into sodium arsenite, sulphur, and water if kept in a closed vessel or when treated with water, and is converted into the trisodium salt on treatment with concentrated sodium hydroxide. The monopotassium salt, obtained by treating the crude tripotassium salt with salicylic acid, crystallises in short needles; the *dipotassium* salt, $K_2HAsSO_3 + 2\frac{1}{2}H_2O$, in colourless, prismatic needles.

Sodium dithioarsenate, $Na_3AsS_2O_2 + 10H_2O$, is obtained by the methods previously described. It is not decomposed by boiling with sodium hydroxide, and only partially so when evaporated to dryness; when heated in a sealed tube at 150° with sodium hydroxide, it yields arsenate and tetrathioarsenate. No precipitate is formed on adding barium chloride to a hot dilute solution of the salt, but, on cooling, a precipitate of lustrous spangles gradually forms. The *potassium* salt, prepared by boiling the tetrathioarsenate with potassium hydroxide, forms small, yellow crystals, is very hygroscopic, and is decomposed by water, yielding potassium arsenate and tetrathioarsenate. E. C. R.

Homogeneity of Helium and Argon. By WILLIAM RAMSAY and J. NORMAN COLLIE (*Proc. Roy. Soc.,* 1896, **60**, 206—216).—See Abstr., 1896, ii, 647.

Attempt to Separate the Two Constituents of Clèveite Gas by Diffusion. By AUGUST HAGENBACH (*Ann. Phys. Chem.,* 1897, [ii], **60**, 124—133).—Helium obtained from clèveite by the action of sulphuric acid on the mineral was submitted to diffusion through a plug of graphite, with the object of effecting a separation of the gas into its two supposed constituents. Spectroscopic examination of the gas as it diffuses through the graphite shows that the yellow D_3 line makes its appearance first of all in the spectrum, and some seconds later the green helium line appears. It is impossible to decide definitely, how-

ever, whether this behaviour is due to diffusion or to the change in the pressure to the gas. Helium was also allowed to diffuse through unglazed porcelain, and the densities of the original gaseous mixture, of the diffusate, and of the residue were determined. The following results were obtained.

	Weight in milligrams.	Volume in c.c. at 0° and 760 mm.	Density, H = 1.
Gaseous mixture ...	20·80	138·20	2·315
Diffusate	8·20	44·84	2·032
Residue..............	10·07	86·60	2·576

The author concludes from the results of his experiments that a separation of clèveite gas into two constituents has been effected. (Compare Ramsay and Collie, Abstr., 1896, ii, 645.) H. C.

Argon, Helium, and Prout's Hypothesis. By BOHUSLAV BRAUNER (*Chem. News*, 1896, **74**, 223—224).—The author inclines to the view that argon and helium are allotropic states of nitrogen and hydrogen of a peculiar and entirely novel character, and suggests that determinations of their specific and atomic heats would throw important light on this question. H. C.

Ammonio-silver Chlorides. By R. JARRY (*Compt. rend.*, 1897, **124**, 288—291).—When an ammoniacal solution of silver chloride is placed in a vacuum, it behaves, at first, like a solution of ammonia only, and the pressure diminishes as the ammonia is removed. When, however, the pressure is reduced to 268 mm., it remains stationary for a time, and 10 to 15 c.c. of liquid may give off 500 c.c. of ammonia without any change of pressure. Beyond this point, the pressure again diminishes gradually until it reaches 17 mm., when it again remains stationary. When the vapour pressure of water is taken into account, these pressures become 263 mm. and 12 mm. respectively. Now these are exactly the respective dissociation pressures of the compounds $AgCl,3NH_3$ and $2AgCl,3NH_3$ at 0° in a dry vacuum, and it follows that the two compounds are successively formed under the conditions specified, and have the same dissociation pressures in solution as in a dry vacuum. This conclusion is confirmed by the solubility of silver chloride in ammonia solution of various degrees of concentration. The following table gives the amounts of ammonia and silver chloride respectively in 10 c.c. of liquid at 0°:

NH_3.........	0·145	0·294	0·560	0·624	1·177	1·636
AgCl	0·049	0·136	0·344	0·400	0·468	0·518
NH_3.........	2·816	2·980	3·019	3·243	3·456	3·748
AgCl	0·659	0·709	0·725	0·587	0·477	0·390

If these results are plotted with the weights of ammonia as abscissæ and the weights of silver chloride as ordinates, the curve shows marked discontinuity at a point which corresponds with the formation of $2AgCl,3NH_3$ (allowance being made for the quantity of ammonia necessary to saturate the water present under a pressure of 12 mm.), and a second break at a point which corresponds with the formation of $AgCl,3NH_3$. Below the first point, the curve represents the solubility

of silver chloride only, between the two points it represents the solubility of the compound $2AgCl,3NH_3$, and beyond the second point the solubility of the compound $AgCl,3NH_3$ under pressures higher than its dissociation pressure.

Other conditions being the same, the solubility of silver chloride in ammonia increases with the temperature; a solution saturated at 20° and cooled to 0°, deposits crystals of the compound $2AgCl,3NH_3$. Highly concentrated solutions deposit the compound $AgCl,3NH_3$. If the solution is represented by a part of the curve beyond the second break, precipitation of the salt is produced by passing a current of ammonia gas into it; if it is represented by a part of the curve between the two breaks, precipitation follows a reduction of the pressure.

C. H. B.

Silver Peroxynitrate. By EDUARD MULDER and J. HERINGA (*Rec. Trav. Chim.*, 1896, **15**, 235—279. Compare Abstr., 1896, ii, 561).—Further quantities of Ritter's black compound have been obtained from solutions of silver nitrate containing from 100 to 1000 grams of the salt per litre, and the authors have succeeded in establishing the anhydrous character of the compound; the different amounts of water given by other experimenters were due in all probability to the fact that, on heating, the compound may explode, and particles can thus pass into the drying tubes. The strength of the original solution appears to have little or no influence on the composition of the black product formed; further analyses agree with the formula, $2Ag_3O_4,AgNO_3$, previously given. More accurate results are obtained when the nitrogen is estimated as silver nitrate rather than as nitrogen by Dumas's method.

The compound slowly undergoes decomposition at the ordinary temperature, whilst, on warming suddenly, oxygen is evolved almost explosively; this oxygen the authors term *oxygen excess*, the amount being 5 atoms for each molecule of the compound. Part of the oxygen excess appears to be given off more readily than the remainder. The residue left consists of a mixture of silver oxide and nitrate, which are best separated by water and not by alcohol. The paper concludes with a short history of the compound.

J. J. S.

Solubility of Calcium Carbonate and Phosphate. By EGIDIO POLLACCI (*L'Orosi*, 1896, **19**, 217—230).—Red litmus paper turns blue when placed in a sludge of pure calcium carbonate, and on leaving pure calcium carbonate in contact with water free from carbonic anhydride for 24—30 hours and filtering, the filtrate has an alkaline reaction towards litmus; on boiling calcium carbonate with water and rapidly filtering, the filtrate slowly deposits calcium carbonate. The author finds that calcium carbonate dissolves in 9662 parts of water at 12°, and in 6904 parts at 100°; Fresenius determined these numbers as 10,601 and 8234 respectively.

One litre of rain water dissolves 0·0216 gram of tricalcium phosphate at 12·5° and 0·0120 gram at 100°; if the water be saturated with carbonic anhydride, it dissolves 0·1605 gram of phosphate at 10·5°. One litre of rain water free from air and carbonic anhydride dissolves 0·0098 gram of the phosphate at 12·5°, but if the phosphate be dried at

25° instead of moist as precipitated, 0·0181 gram is dissolved. Water saturated with carbonic anhydride dissolves 0·0450 gram of calcium phosphate and 0·3650 gram of calcium carbonate per litre at 13·5° if agitated with a mixture of the salts.

Since many plants contain much lime, a constituent in which many earths are poor, the author recommends that calcium salts, such as the sulphate or carbonate, and lime should be applied as a manure, as the addition of these substances may sometimes give better results than that of calcium phosphate. W. J. P.

The So-called "Hypoiodite of Magnesia." By JAMES WALKER and SYDNEY A. KAY (*Proc. Roy. Soc. Edin.*, 1896, 235—248).—When magnesia is shaken up with iodine, it unites with the latter and assumes a deep brown colour (Gay-Lussac). The same brown colour is produced, whether the magnesia is freshly precipitated, dried at 100°, or ignited over the blow-pipe, and whether the iodine is in the form of vapour, or in solution in water, aqueous potassium iodide, chloroform, carbon bisulphide, or alcohol. Traces of iodine vapour are given off from the brown substance, even at the ordinary temperature, but heating for several hours at 350° is not sufficient to expel all the iodine. At a red heat, iodine is given off rapidly, and magnesia remains. Chloroform, carbon bisulphide, and carbon tetrachloride, at the temperatures of their boiling points, extract iodine from the "hypoiodite" only very slowly. Water decomposes it, slowly at the ordinary temperature and rapidly on boiling, with formation of magnesium iodide and iodate. Quantitative experiments were made, to determine the relation between the amount of iodine absorbed by the magnesia and the concentration of the iodine solution in which the absorption occurred. With aqueous potassium iodide as solvent, no definite results could be obtained, owing to the disturbing effect of the chemical action of the water. In anhydrous chloroform, the amount absorbed diminished with the final concentration of the solution, but much less rapidly than this. The authors consider that the formation of the "hypoiodite" is analogous to cases of absorption, such as that of acids by silk, or of iodine by starch (compare Walker and Appleyard, Trans., 1896, 1334; Küster, Abstr., 1895, i, 199). J. W.

Action of Cuprous Oxide on Silver Nitrate Solutions. By PAUL SABATIER (*Compt. rend.*, 1897, **124**, 363—366).—When cuprous oxide is treated with successive quantities of silver nitrate solution, until no more copper is dissolved, and the residue is washed with cold water and dried by exposure to air, the product is a greenish-grey powder consisting of a mixture of basic copper nitrate and metallic silver, part of the latter being filiform; it has the composition, $Ag_6 + Cu(NO_3)_2,3CuO,3H_2O$, one-third of the nitric acid of the silver nitrate being found in the precipitate. If the silver nitrate solution is hot, the product is practically the same.

The grey mixture is insoluble in cold water, but when treated with boiling water, some cupric nitrate is dissolved, but the solution contains no nitrite. Nitric acid dissolves it readily and completely; concentrated sulphuric acid attacks it violently, with the formation of copper nitrosodisulphonate (Abstr., 1896, ii, 599, 622, 641) in consequence of the reducing action of the metallic silver on the sulphuric acid and

liberated nitric acid; dilute sulphuric acid dissolves all the copper and part of the silver; acetic acid behaves similarly, but dissolves very little silver; hydrochloric acid dissolves all the copper, and leaves a residue of violet-coloured, silver chloride. C. H. B.

Silicides of Copper and Iron. By GUILLAME J. L. DE CHALMOT (*Amer. Chem. J.*, 1897, **19**, 118—123).—The author finds that the crystalline copper silicide of the composition Cu_2Si_3 previously described by him (Abstr., 1896, ii, 362) is not a true chemical compound, but a mixture of silicon, copper silicide, and copper, the copper silicide present never containing more silicon than is represented by the formula Cu_2Si. In the case of a silicide containing excess of silicon, there is less silicon united with copper than would be the case if the latter were present only in the form of Cu_2Si. In order to prove whether a part of the copper is present as a silicide containing less silicon or in the free condition, some of the crystals were triturated with mercury in a mortar. After filtering through linen and evaporating the mercury, a residue of cuprous oxide was left. Evidently, therefore, free copper, free silicon, and copper silicide can exist side by side in the electric furnace..

A silicide of iron having the composition $FeSi_2$ is also described, obtained in grey, metallic crystals by treatment with small quantities of hydrofluoric acid of an iron-silicon alloy containing about 39 per cent. of silicon. A. W. C.

Action of Carbonic Anhydride and Carbonic Oxide on Aluminium. By ANTOINE GUNTZ and ARTHUR MASSON (*Compt. rend.*, 1897, **124**, 187—190).—It is known that aluminium becomes incandescent when heated in a mixture of carbonic anhydride and iodine vapour, and this is generally attributed to the combination of the halogen with the metal. The authors find, however, that a considerable absorption of carbonic anhydride takes place, and that the incandescence is more intense if carbonic oxide is substituted for the anhydride, but does not take place at all in a mixture of iodine vapour and hydrogen. When heated in carbonic anhydride only, finely-powdered aluminium is, as a rule, only slightly affected, but the commercial powder often becomes incandescent, and the product evolves considerable quantities of methane when treated with water. If the aluminium is heated to dull redness in carbonic oxide or anhydride containing a small quantity of the vapour of aluminium chloride or iodide, the metal readily becomes incandescent, and is more or less completely converted into the carbide Al_4C_3 which yields methane on treatment with water. C. H. B.

Action of Nitrogen Oxides on Ferrous Chloride and Bromide. By VICTOR THOMAS (*Compt. rend.*, 1897, **124**, 366—368).—Ferric bromide is reduced more readily than the chloride by nitric oxide with formation of ferrous bromide and nitrosyl bromide, and the ferrous bromide absorbs nitric oxide; but whether the compound has the composition $5Fe_2Br_4,NO$ or $6Fe_2Br_4,NO$ has not yet been definitely ascertained. It does not alter in dry air, nor does it lose nitric oxide in a vacuum. Ferrous bromide in solution absorbs nitric oxide in the same way as other ferrous salts, but the compound

formed has not yet been isolated, although it seems to be crystallisable.

Ferrous chloride or bromide readily absorbs dry nitric peroxide, the compound formed being $2Fe_2Cl_4,NO_2$, or $2Fe_2Br_4,NO_2$. Both compounds are stable when exposed to air, and do not lose nitrogen peroxide in a vacuum. In most reactions, however, they split up into a mixture of ferrous salt and nitrogen peroxide. When dissolved in water, for example, alkalis precipitate black iron oxide from the solution.

In presence of moisture, the two ferrous salts seem to absorb even larger quantities of nitric peroxide, but the reaction is complicated, and some chlorine (or bromine) is removed. C. H. B.

Organic Compounds which prevent the Precipitation of the Hydroxides of Iron, Nickel, and Cobalt. By JAN ROSZKOWSKI (*Zeit. anorg. Chem.*, 1897, 14, 1—20).—Of 111 organic compounds which were examined, only 25 prevent precipitation of the hydroxides of these metals, and these compounds belong to the polyacid alcohols, the carbohydrates, the hydroxy-monobasic or polybasic acids, and in a few cases to the amido-acids, the poly-acid phenols, and the phenolic acids. The monobasic and polybasic organic acids prevent the formation of the hydroxides only in acid or neutral solutions; in alkaline solutions, a precipitate is nearly always obtained, although it is often some time in forming. Most of the organic compounds which prevent the formation of the hydroxides belong to the fatty series, and the corresponding aromatic compounds, with a few exceptions, are without influence. These, also, all contain the hydroxyl group, and if this group is replaced by another monatomic basic or acid group, the compounds formed are without influence, except in the case of the amido-compounds, which form soluble complex salts with copper and nickel.

These organic compounds have a very varying influence on the precipitation of the hydroxides. Of 25 compounds, 22 prevented the precipitation of hydroxide from a solution of ferric chloride; and only 9 prevented the precipitation of hydroxide from ferrous sulphate. The capability of forming complex soluble compounds increases with the number of the hydroxyl groups; the monhydric alcohols are without influence on the precipitation; but, commencing with glycol, the influence is proportional to the number of the hydroxyl groups.

E. C. R.

Nomenclature of Ammonio-cobalt Compounds. By ALFRED WERNER (*Zeit. anorg. Chem.*, 1897, 14, 21—27).—Those atoms, or groups of atoms, which form with the metal a complex radicle, are placed before the name of the metal in the following order: first, the name of the acid-residue, then the groups similar to the ammonia group, and immediately preceding the name of the metal the ammonia (ammino) groups. The ammonia group is designated by the word *ammine*, to distinguish it from the *amine* of organic compounds. All other groups and atoms which do not belong to the complex radicle are placed after the name of the metal. In the case of isomeric compounds, the author numbers the groups comprised in the complex with the angles of the octahedron which they occupy in relation to the metallic atom in accordance with his theory.

Those names which refer to the colour of the compounds are not employed. A few examples are given below.

New name.	Formula.	Old name.
Hexamminocobalt salts	$[Co(NH_3)_6]X_3$	Luteocobalt salts.
Aquopentamminocobalt salts	$[Co(NH_3)_5OH_2]X_3$	Roseocobalt salts.
Nitritopentamminocobalt salts	$[Co(NH_3)_5NO_2]X_2$	Xanthocobalt salts
1 : 6-Dichlorotetramminocobalt salts	$[Co(NH_3)_4Cl_2]X$	Dichloropraseo-cobalt salts.
1 : 2 : 4-Trinitritotriammine cobalt	$Co(NH_3)_3(NO_2)_3$	Triaminecobalt nitrite [(Gibbs').
1 : 2 - Dinitritotetramminocobalt salts ...	$[Co(NH_3)_4(NO_2)_2]X$	Flavocobalt salts.

E. C. R.

1 : 6-Dichlorotetramminocobalt Salts (Chloropraseo-salts). By ALFRED WERNER and ARNOLD KLEIN (*Zeit. anorg. Chem.*, 1897, **14**, 28—41).—*Dichlorotetramminocobalt hydrogen sulphate* $(Co(NH_3)_4Cl_2)\cdot SO_4H$, is prepared by treating the solid carbonatotetrammine chloride, $Co(NH_3)_4CO_3Cl$, with concentrated hydrochloric acid in a freezing mixture, dissolving the product in concentrated sulphuric acid, and adding hydrochloric acid as long as a precipitate is formed; the mixture is then allowed to remain for a few days in a closed flask, and the precipitate collected and washed with alcohol and ether; it is easily purified by dissolving it in water and precipitating with dilute sulphuric acid. It crystallises in beautiful, dark green needles, is easily soluble in water, and has a strongly acid reaction. With hydrochloric acid and chlorides, it yields a bright green, crystalline precipitate of dichlorotetramminocobalt chloride; it is decomposed by mercurous nitrate, potassium cyanide, and potassium ferrocyanide, and dissolves in concentrated sulphuric acid with a red coloration and evolution of hydrogen chloride. It is more stable in aqueous solution than the other salts of the series, but the colour of the solution gradually changes to blue, violet, becomes colourless, and finally red. When the concentrated aqueous solution is warmed, a precipitate of chloraquotetramminocobalt sulphate, $[Co(NH_3)_4ClH_2O]SO_4$, is obtained in the form of lustrous, reddish-violet plates; this dissolves in concentrated sulphuric acid with a violet coloration, and when treated with concentrated hydrochloric acid in aqueous solution, yields chloraquotetramminocobalt chloride. The *silver* salt, $[Co(NH_3)_4Cl_2]SO_4Ag$, is obtained as a flocculent, bright green precipitate by mixing solutions of equivalent quantities of the hydrogen sulphate and silver nitrate at a low temperature. The *bismuth* salt, $Bi[Co(NH_3)_4Cl_2SO_4]_3$, is obtained in a similar way as a green, pulverulent precipitate. The *chloride*, $[Co(NH_3)_4Cl_2]Cl$, *bromide, iodide, fluoride, nitrate, nitrite, thiocyanate, platinochloride, platinosochloride, aurochloride, dichromate, chromicyanide,* and *ferricyanide* are also described. With mercuric chloride, potassium- and dipotassium-mercuric chloride, varying mixtures of salts are obtained according to the conditions, but the authors were unable to isolate a pure salt.

A cobalt ammonium sulphite compound is described by Vortmann and Magdeburg (Abstr., 1890, 14), which, according to its method of pre-

paration, should belong to the 1 : 6-dichlorotetrammine salts; the authors have repeated this experiment, and obtained a compound which is not a dichlorotetrammine salt. They are engaged in further investigations.

E. C. R.

Chromium and Manganese Phosphides. By A. Granger (*Compt. rend.*, 1897, **124**, 190—191).—Chromic chloride is reduced to chromous chloride when heated with phosphorus in presence of carbonic anhydride, but no phosphide is formed. Manganous chloride can be volatilised in phosphorus vapour without any decomposition taking place. If, however, the carbonic anhydride is replaced by hydrogen, *chromous phosphide*, CrP, and *manganous phosphide*, Mn_3P_2, are formed respectively, a result probably due to an intermediate formation of hydrogen phosphide.

Chromous phosphide is a grey solid with a graphitoidal appearance; it is not affected by aqua regia. Manganous phosphide forms highly lustrous, slender needles, and is attacked by aqua regia. Neither compound is affected by nitric acid, but both are readily attacked by chlorine, with incandescence, and both are slowly oxidised when heated in air. They are also decomposed by fused potassium hydroxide.

C. H. B.

Mineralogical Chemistry.

Molybdenum, Selenium, &c., in Coal from Liége. By ARMAND JORISSEN (*Ann. Soc. Geol. Belgique,* 1896, **23**, 101—105).—The brownish-grey flue-dust, produced when Liége coal is burnt, contains ammonium salts, sulphates, and iron; and in the aqua regia extract, traces of the following were found, Se, Mo, Sb, Bi, Ni, Co, As, Cu, Pb, Zn, Ca. L. J. S.

Artificial Antimonite [Stibnite] and Bismuth Crystals. By P. PHILIPP HEBERDEY (*Ber. Akad. Wien,* 1895, **104**, i, 254—266).—Crystals of stibnite are described from a specimen of slag from the smelting works of Przibram in Bohemia; they attain a length of 1 cm., and are found in drusy cavities in a material which is shown by analysis to be mainly a mixture of Fe_2S and Cu_2Sb. Other layers of this specimen are shown by analysis to consist of mixtures of metasilicates and sulphides.

Acicular crystals of bismuth from another furnace product from Przibram are of unusual habit; they consist of elongated hexagonal prisms, $b\{2\bar{1}\bar{1}\}$, with irregular terminations showing the forms $o\{111\}$, $e\{011\}$, $s\{\bar{1}11\}$. There is a perfect cleavage parallel to b, a good one parallel to o, and others, less distinct, parallel to e and s. L. J. S.

A Tellurium Mineral from Colorado. By RICHARD PEARCE (*Proc. Colorado Sci. Soc.,* 1896, [Oct. 5th], pp. 2).—A dark grey mineral, with bright, metallic lustre, from the Griffith mine, near Georgetown, was freed as far as possible from intermixed pyrites, galena, copper pyrites, and magnesite, and analysed by F. C. Knight; it gave

Ag.	Te.	Pb.	Cu.	Fe.	Bi.	S.	$MgCO_3$.	Au, Ag.	Insol.	Total.
50·65	18·80	9·34	4·65	4·00	1·16	8·06	1·95	0·48	1·07	100·16

After deducting impurities, this corresponds with a mixture of two parts of hessite (Ag_2Te) and one of argentite (Ag_2S). The gold exists as an alloy with silver. L. J. S.

[Bismutosmaltine, Wolframite, Agricolite, &c.] By AUGUST FRENZEL (*Tscher. Min. Mitth.*, 1897, **16**, 523—529).—The bismuth veins of Zschorlau, Schneeberg, Saxony, carry native bismuth, bismuthic ochre, several uranium minerals, and the following new mineral, to which the name *bismutosmaltine* is given. The last was found in a large nodule of dark blue-grey ore which assayed 40·5 per cent. Bi, and 6·6 Cu; the small cubic crystals are apparently holohedral with the forms $a\{100\}$, $o\{111\}$, $d\{110\}$; the colour is tin-white; strong metallic lustre; streak-black; brittle; H = 6, sp. gr. 6·92. Analysis of pure hexahedral crystals, free from native bismuth, gave

Bi.	Cu.	As.	Sb	Co.	Fe.	S.	Total.
20·17	0·69	61·59	0·16	13·70	3·71	0·05	100·07

The copper and sulphur are due to the presence of copper pyrites, deducting these, $Bi + As + Sb : Co + Fe = 3·07 : 1$, giving the formula $Co(As,Bi)_3$. This is like skutterudite, but with some arsenic replaced by bismuth; the tin-white colour of the mineral is more like the colour of smaltite than that of skutterudite. Cheleutite ("wismuthkobalterz") is related to this, although it is usually considered as a variety of smaltite containing native bismuth.

Wolframite crystals are described from Uncia (prov. Chayanta), Oruro, and Chorolque, in Bolivia. The habit varies considerably; sometimes, by the development of the three axial planes, the crystals have a cubic appearance. Bismuth minerals occur on the specimens. Analysis of material from Uncia, of sp. gr. 6·96, gave

WO_3.	SnO_2.	FeO.	MnO.	Insol.	Total.
73·42	—	18·57	6·64	1·16	99·79
71·68	0·65	19·68	6·20	1·70	99·91

Agricolite is described from a new locality, namely Schwarzenberg, Saxony; it here occurs on bismuthic ochre as radial aggregates, of a greyish yellow or green colour, and resembles wavellite. An oblique extinction of 51° was observed; and besides bismuth silicate, traces of phosphoric acid were found.

Copper glance from the Freiberg district is mentioned as containing 2 per cent. of silver. Pseudomorphs of copper glance after mispickel and of stilpnosiderite after uranite are described. Arsenic rhombohedra are described from Nagyag and Japan; the sp. gr. of the latter is 5·70. L. J. S.

The so-called Dicksbergite. By MATS WEIBULL and AUG. UPMARK (*Geol. För. i Stockholm Förh.*, 1896, **18**, 523—526).—A mineral from Dicksberg, parish of Ransäter, Wermland, recently described by L. J. IGELSTRÖM (*Geol. För. Förh.*, 1896, **18**, 231) as a new mineral, under the name of dicksbergite, crystallising in the orthorhombic system and containing titanic acid, thorium, iron, cerium, didymium, yttrium, tin, and tungsten, is here shown to be merely rutile. Besides 98·13 per cent. TiO_2, iron alone is present; the sp. gr.

of 4·20, and the optical and crystallographic characters agree with those of rutile. L. J. S.

Monazite. By H. B. C. Nitze (*16th Ann. Rept. U.S. Geol. Survey for* 1894—5, 1895, part iv, 667—693).—This is a monograph of the mineral, and gives a summary of the history, and of the crystallographic, physical, and chemical characters; the known localities are enumerated, and a bibliography is added; the uses and methods of extraction are also described. Thirty-seven analyses are quoted. Monazite sand, containing up to about 67 per cent. of monazite, from North Carolina, contains, according to analyses by C. Baskerville, 0·125 to 6·54 per cent. of thoria. L. J. S.

[Mispickel, Vivianite, &c., from Bohemia.] By Friedrich Katzer (*Tscher. Min. Mitth.*, 1897, **16**, 504—518).—Massive, granular mispickel from a deposit in decomposed red granite near Sestrouň, north-east of Selčan, gave the following results on analysis; II was made in the k.k. geol. Reichsanstalt.

	S.	As.	Fe.	Au.	Ag.	Total.	Sp. gr.
I.	19·96	45·53	33·66	trace	nil	99·15	6·179
II.	—	34·40	—	0·0012	0·0014	—	—

Vivianite occurs in pegmatite at Kloub, near Protiwin, as earthy crusts of a sky-blue colour; it is at first almost white (sp. gr. 2·658), but, on exposure, soon becomes greenish, and finally blue. In larger cavities, there are good crystals (sp. gr. 2·587) of a light greyish-green colour, but they become blue on exposure to air. The percentages of water found in the earthy variety, arranged according to the intensity of the blue colour and commencing with the lightest, were 27·33, 27·65, 27·12, 28·12, 28·66, mean 27·77; this indicates that the change in colour is connected with the absorption of water from the air. Crystals gave, 27·08, 26·68 and 26·99, mean 26·92, per cent. of water, and 3·08 Fe_2O_3, 41·12 FeO per cent. As regards the origin of the vivianite, it could have been derived from the apatite in the pegmatite, or have been deposited by infiltering organic matter; the latter is the more probable.

Crystals of mimetite are described from Hodowitz; sp. gr. 7·126; 75·12 per cent. Pb. Descriptions are also given of crystals of calcite; of an occurrence of anthracite with quartz in porphyry; and of an occurrence in sandstone of viscous petroleum of sp. gr. 0·92. L. J. S.

Munkforssite, Bliabergite and Ransätite, Three New Swedish Minerals. By Lars J. Igelström (*Zeit. Kryst. Min.*, 1897, **27**, 601—604)—In the gneiss of the parish of Ransäter, in Wermland, are thick bands of quartz, which is quarried at Bliaberg and Dicksberg for the preparation of a refractory material for the iron furnaces of Munkforss. In the white quartz are plates of damourite, bands of pyrites, also apatite, zircon, kyanite, ilmenite, and the three new minerals described below.

Munkforssite occurs in kyanite at Dicksberg; it is white, then resembling quartz, or sometimes pale reddish, and is transparent to translucent. It occurs as grains, and as "monosymmetric" crystals. It is infusible, and is only partially decomposed by acids. In the closed tube, it gives only a trace of acid water. The results of the

analysis are given under I; deducting the undecomposed portion (damourite), and adding the loss on ignition to the SO_3, the composition of the mineral is given under II.

	SO_3.	P_2O_5.	Al_2O_3.	CaO.	FeO.	Cl.	Loss on ignition.	Insol.	Total.
I.	13·20	13·98	25·54	32·00	trace	trace	2·63	10·74	98·09
II.	18·12	16·01	29·23	36·64	—	—	—	—	100·00

This somewhat resembles the rhombohedral svanbergite in composition. The pale green *kyanite*, which contains the munkforssite, gave SiO_2, 43·91; Al_2O_3, 56·52; FeO, trace = 100·43 per cent.

Bliabergite (spelt bliabergsite in *Geol. För. Förh.*, 1896, **18**, 41).—This occurs plentifully in the white damourite of Bliaberg as "rhombohedral" crystals, which when fresh are almost black (anal. I), but when weathered are more or less red (anal. II). H = 4·5. It is infusible, and is only partially decomposed by acids.

	SiO_2.	Al_2O_3.	FeO.	MnO.	MgO,CaO.	$Fe_2O_3(Mn_2O_3)$	H_2O.	Total.
I.	39·13	27·60	26·74	4·45	0·43	—	3·26	101·61
II.	41·67	23·81	—	—	—	27·38	7·14	100·00

From I is deduced the formula $2(Fe,Mn)_2SiO_4 + Al_4Si_3O_{12}$, or $3(Fe,Mn)_2SiO_4 + 2Al_2SiO_5$; and from II, $Al_4Si_3O_{12} + 2H_2O$. [M. Weibull (*Geol. För. Förh.*, 1896, **18**, 515) shows this to be near ottrelite].

Ransätite (*Geol. För. Förh.*, 1896, **18**, 43), also from the damourite of Bliaberg, occurs as pale red, globular masses. The crystal system is given as cubic. H = 6. Before the blow-pipe, it becomes black and is infusible; insoluble in acids. Analysis gave

SiO_2	Al_2O_3	Fe_2O_3.	MnO.	CaO.	MgO.	Total.
43·47	14·50	17·72	14·97	5·63	2·57	98·86

The formula is given as $3(Mn,Ca,Mg)SiO_3 + (Fe,Al)_4Si_3O_{12}$.

L. J. S.

Artificial Gypsum. By L. Jowa (*Ann. Soc. Geol. Belgique*, 1896, **23**, pp. cxxviii—cxxx).—Cesàro has previously obtained small crystals of gypsum by allowing a solution of ferrous sulphate, in contact with the air, to act on chalk. The present author has kept the same materials for four months in a long necked flask; by retarding the rate of oxidation of the ferrous sulphate in this way, good crystals have been obtained. The pieces of chalk become coated with ferric hydroxide and acicular gypsum crystals. The crystals show the forms *b* {010}, *m* {110}, *l* {111}; the largest, 1 cm. long, are elongated in the direction of the vertical axis, but others are elongated in the direction of the edge [111, $1\bar{1}1$]. Twin crystals, with *a*(100) the twin plane, are also present. L. J. S.

Leonite from Leopoldshall. By C. August Tenne (*Zeit. deut. geol. Ges.*, 1896, **48**, 632—637).—The artificial salt, $MgSO_4,K_2SO_4 + 4H_2O$, has been prepared artificially by van der Heide (Abstr., 1893, ii, 276) who named it potassium-astrakanite; and the natural mineral from Westeregeln, where it has been known at the salt works since 1889, has been described by Naupert and Wense (Abstr., 1893, ii, 325), and analysed by Geserich, who found

K_2SO_4.	$MgSO_4$.	Na_2SO_4.	NaCl.	$MgCl_2$.	H_2O.
40·2—45·3	32·0—34·3	1·3	0·5—3·5	0·3—4·8	19·3—20·7

As shown in the present paper, there is no crystallographic relation between this mineral and blödite (= astrakanite, $MgSO_4,Na_2SO_4 + 4H_2O$), so that the older but unpublished name, leonite, is used in preference to kaliblödite or kaliastrakanite. At Leopoldshall, near Stassfurt, the mineral occurs as thick, tabular crystals, along with kainite and rock salt; the colour is faintly yellowish, but sometimes reddish, greyish, or bright canary yellow. Between these large, indistinct crystals are kieserite and thin, colourless, monosymmetric crystals of leonite, tabular parallel to c{001} and with many small planes at the edges; $a : b : c = 1·03815 : 1 : 1·23349$; $\beta = 84° 50'$. The optic axial plane is perpendicular to the plane of symmetry, and makes an angle of 29½° with the base. There is no distinct cleavage; fracture conchoidal. It is soluble in water; analysis by Braun gave

Mg.	K.	SO_4.	Cl.	H_2O.	Insol.	Na.	Total.
6·54	25·48	43·73	4·84	18·99	0·42	nil	100·00

Deducting 10·16 per cent. of KCl as impurity, this gives $MgSO_4,K_2SO_4 + 4H_2O$. The small, colourless crystals contained no chlorine.

L. J. S.

Wolframite from Argentina. By GUILLERMO BODENBENDER (*Zeit. Kryst. Min.*, 1896, **27**, 533—534; from *Zeit. prakt. Geol.*, 1894, 409—414).—Wolframite occurs with apatite, copper pyrites, molybdenite, fluorite, scheelite, mica, and chlorite in granite, and in the quartz veins of the neighbouring gneiss near to Sauce, Dept. Calamuchita, not far from the crest of the Sierra de Córdoba. Analysis of the wolframite gave

WO_3.	Nb_2O_5.	FeO.	MnO.	Total.
74·86	1·22	13·45	11·02	100·55

Here Fe : Mn = 4 : 3. L. J. S.

Meerschaum from Eskishehir, Asia Minor. By ERNST WEINSCHENK (*Zeit. Kryst. Min.*, 1897, **27**, 574—576).—The composition of meerschaum is somewhat uncertain, as different analyses show varying amounts of water. The material from Eskishehir, examined by the author, is seen under the microscope to be a compact, fibrous aggregate with weak birefringence. The air-dried material loses 14·35 per cent. over sulphuric acid, at 210° there is a further loss of 0·88 per cent., and up to 300° there is no more loss; material which has been heated up to 300° retains its original optical character, so that the water lost below this temperature must be considered to be hygroscopic, and contained in the fine pores of the mineral. The water directly determined on material dried at 210° amounted to 12·10 per cent.; this corresponds with the formula $H_4Mg_2Si_3O_{10}$. In Asia Minor, meerschaum occurs associated with magnesite veins in serpentine, but it has probably not been derived from the magnesite. L. J. S.

[Halotrichite, Dioptase, and Rhodochrosite from Argentina.] By GUILLERMO BODENBENDER (*Bol. Acad. Cien. Córdoba*, 1894, **14**, 110—115).—The shores of a lake on the slopes of the volcano of Copahué are coated with an efflorescence of a white, porous material having a granular or fibrous structure, with delicate needles in places (I); another sample is pulverulent and without needles (II). Sulphur occurs mixed with the salts, this being deposited from the hot water

of the lake, which is charged with hydrogen sulphide. Lemon-yellow coquimbite is also present.

	SO_4.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	H_2O.	Total.
I.	41·203	12·234	6·639	trace	trace	40·010	100·086
II.	35·509	13·012	0·681	0·674	0·236	[49·888]	100·000

The iron is partly as FeO, and one determination gave 1·098 per cent. FeO. The composition of the deposit is variable, and, as seen from the analyses, differs somewhat from that of halotrichite.

Dioptase occurs in a quartz vein in gneiss in the Sierra Chica, Córdoba, as prismatic crystals with rhombohedral terminations, the largest measuring 12 × 5 mm.; more often it occurs as a thin incrustation, or filling fissures; it is associated with linarite, malachite, azurite, cerussite, and chrysocolla. As crystals were plentiful, the following analysis was made.

SiO_2.	CuO.	Fe_2O_3.	H_2O [diff.].
38·384	50·674	0·674	[10·266]

Rhodochrosite, which occurs with galena, blende, and barytes at Capillitas in Catamarca, varies considerably in colour, texture, and composition. It is usually concretionary, but is sometimes found as small rhombohedra of a reddish colour; analysis II was made on material showing some crystals.

	$MnCO_3$.	$CaCO_3$.	$FeCO_3$.	$MgCO_3$.	Total.
I.	90·099	3·913	3·614	2·451	100·077
II.	93·064	2·658	2·843	2·106	100·671

A greyish-white compact specimen contained only 62 per cent. $MnCO_3$. Vivianite from Córdoba is also described. L. J. S.

Mineral Veins in the Serpentines of the Austrian Alps. By ERNST WEINSCHENK (*Zeit. Kryst. Min.*, 1897, **27**, 559—573).—It is pointed out that in the mineral veins which occur in connection with the serpentines of the East Central Alps (this vol., ii, 106), magnesium minerals are of somewhat exceptional occurrence; in the present paper, occurrences of olivine and serpentine in veins in the stubachite (*Abhand. k. bayer. Akad. Wiss.*, II Cl., 1894, **18**, 653) of the Stubachthal are described. The olivine, when it is embedded in calcite, is present as good crystals; analysis by Vötter gave

SiO_2.	FeO.	MgO.	TiO_2.	Total.	Sp. gr.
39·69	12·43	48·33	nil	100·45	3·357

The optic axial angle is very near to 90°.

In calcite veins, in the serpentine of Scheidmoosgraben near Bruck, are radial aggregates of aragonite which somewhat resembles hydromagnesite in appearance; analysis gave

CaO.	MgO.	Loss on ignition.	H_2O.	Sp. gr.
55·68	0·20	43·82	1·00—1·29	2·900

In connection with this, the aragonite and hydromagnesite of Texas, Pennsylvania, were examined. L. J. S.

Augite Crystals from the Central Plateau [of France]. By FERDINAND GONNARD (*Zeit. Kryst. Min.*, 1897, **27**, 614; from *Bull. soc. fran. min.*, 1895, **18**, 99—105).—Augite crystals from various

localities are described. Isolated, simple, and twinned crystals of the usual combination, from the lapilli-tufts of Puy de la Rodde, Puy-de-Dôme, gave, on analysis by Pisani,

SiO_2.	CaO.	MgO.	FeO.	Al_2O_3.	K_2O,Na_2O.	Loss on ignition.	Total.	Sp. gr.
47·10	20·25	12·70	9·60	10·20	0·84	0·20	100·89	3·266

L. J. S.

Fuggerite, a New Mineral from the Fassathal. By ERNST WEINSCHENK (*Zeit. Kryst. Min.*, 1897, **27**, 577—582).—This occurs with calcite in a hornfels close to the monzonite contact. The fresh, apple-green crystals are thick, tetragonal tables, and closely resemble gehlenite in appearance, but have a perfect basal cleavage, and are slightly harder and denser than the latter mineral. It is very easily decomposed, with separation of pulverulent silica, by dilute hydrochloric or organic acids, or even on long standing in distilled water. The specific gravity of the crystals, which, however, contain a little calcite, is 3·175—3·180. Material for analysis was separated by heavy liquids, and purified from calcite by the action of hydrochloric acid. The following results were obtained by E. Mayr.

SiO_2.	Fe_2O_3.	Al_2O_3.	MgO.	CaO.	Na_2O.	Total.
34·03	3·54	17·74	4·90	37·75	2·04	100·00

This agrees with a mixture of 10 molecules of gehlenite and 3 of åkermanite; but as the physical characters differ from those of Vogt's gehlenite-åkermanite group, fuggerite must be considered to belong to a dimorphous group, which is probably also tetragonal. For sodium light, fuggerite is isotropic, with a refractive index of 1·691, and for other colours the double refraction is exceedingly small; sections perpendicular to the base show a dark blue tint between crossed nicols.

L. J. S.

Manganandalusite from Vestanå. By HELGE BÄCKSTRÖM (*Geol. För. i Stockholm Förh.*, 1896, **18**, 386—389).—This new variety of andalusite is of wide distribution in the quartz-muscovite- and kyanite-schists in the neighbourhood of Vestanå, N.E. Scania. It occurs as grains of a grass-green colour, and only differs from ordinary andalusite in the high content of manganese and in the remarkable strength of the pleochroism; even in thin rock sections, the pleochroism is very marked, with $a = \mathfrak{c}$ and $b = \mathfrak{b}$ blue-green, and $c = \mathfrak{a}$ intense pure yellow. Analysis by H. Santesson gave

SiO_2.	Al_2O_3.	Mn_2O_3.	CaO.	Fe_2O_3.	Total.
36·72	56·99	6·91	trace	nil	100·62

This agrees with the formula $(Al,Mn)_2SiO_5$. The largest amount of manganese previously found is 0·83 per cent. Mn_2O_3, this being in andalusite from Lisens Alp, Tyrol, analysed by Erdmann. The green andalusite of Brazil contains no manganese, and is not so pleochroic as the mineral here described. L. J. S.

Clay. By HEINRICH RIES (*16th Ann. Rept. U.S. Geol. Survey, for* 1894—5, 1895, part iv, 523—575).—In this paper, which is on the technology of the clay industry, 450 analyses of kaolin and various kinds of clays are given or quoted. L. J. S.

Meteoric Iron from Locust Grove, North Carolina. By EMIL W. COHEN (*Ber. Akad. Berlin*, 1897, 76—81).—This iron, weighing $10\frac{1}{3}$ kilos. was found on July 29, 1857, at Locust Grove, Henry Co., and had been kept at a house in Georgia until 1895. A bright meteor was seen in the locality on June 26, 1857, but the very thin coating of rust on the surface of the iron is probably more than would have been formed in three days. The structure is granular, with an absence of octahedral and twin lamellæ; the etched surfaces of the grains show numerous minute, rounded elevations. In the outer portion of the meteorite, nodules of graphite and troilite and a platy phosphide of iron and nickel are present, whilst in the central portion there is rhabdite. Analysis by O. Sjöström gave,

Fe.	Ni.	Co.	Cu.	C.	S.	P.	Cl.	Total.	Sp. gr.
94·30	5·57	0·64	trace	0·02	0·05	0·18	0·01	100·77	7·7083

This corresponds with the following mineralogical composition,

Kamacite.	Fe_2NiP.	Troilite.	Lawrencite.
98·70	1·16	0·12	0·02

L. J. S.

Stony Constituents of the Meteoric Iron of Toluca, Mexico. By E. A. HUGO LASPEYRES (*Zeit. Kryst. Min.*, 1897, **27**, 586—600).—A microscopical examination of this iron (*Zeit. Kryst. Min.*, 1895, **24**, 485) has pointed to the probable presence of zircon, quartz, plagioclase, orthoclase, garnet, augite, olivine and apatite. To obtain chemical proofs of the presence of these, 585 grams of the rust was treated with hydrochloric acid, &c.; there then remained an insoluble residue weighing 1·6100 gram, of this, 0·00125 was insoluble in a mixture of hydrofluoric and sulphuric acids, the remainder consisting, as calculated from the analysis, of

Orthoclase.	Plagioclase.	Augite.	Quartz.	Total.
2·45	25·26	37·40	34·89	100·00

Traces of copper, tin, nickel, cobalt, and titanium were also found in the hydrofluoric acid solution. The insoluble portion consisted of cosmochlore, well-developed crystals most probably of zircon, chromite, and some undetermined splinters.

Cosmochlore (kosmochlor) is the name given to small, emerald-green crystals which are probably monosymmetric; the angle of optical extinction on the perfect cleavage parallel to the plane of symmetry makes an angle of 12° 14′ with the trace of a good cleavage which is perpendicular to the last; the substance is strongly pleochroic; it is infusible, and has a sp. gr. greater than 3·158. The result of an analysis on 0·0033 gram is given as:

SiO_2.	Al_2O_3.	Cr_2O_3.	Fe_2O_3.	CaO.	MgO.	Total.
31·82	9·09	39·39	9·09	6·06	4·55	100·00

A formula representing a basic orthosilicate is given. To obtain 1 gram of cosmochlore, 80 kilos. of the meteorite would have to be dissolved.

L. J. S.

Composition of the Gas Evolved from the Water of a Well near Enkhuisen. By M. VAN BREUKELEVEEN (*Rec. Trav. Chim.*, 1896, **25**, 280—281).—The gas examined had the following composition, methane, 82·9; carbonic anhydride, 10·8; nitrogen, 6·3 per cent. by

volume. Its specific gravity = 0·6936. The gas thus agrees in composition with gases obtained from other wells in the same district (compare Oudemans, Jun., *Ann. Phys. Chem.*, **142**, 273).

J. J. S.

Physiological Chemistry.

Argon and Nitrogen in the Blood. By PAUL RÉGNARD and TH. SCHLŒSING, Jun. (*Compt. rend.*, 1897, **124**, 302—304).—Blood was drawn from the jugular vein of a horse in such a manner as to avoid any contact with air, and the dissolved gases were extracted in a vacuum, passed successively over potassium hydroxide and red hot copper, and afterwards examined for nitrogen and argon. Each litre of blood was found to contain 0·42 c.c. of argon and 19·98 c.c. of nitrogen.

The authors also determined the solubility of chemical nitrogen and argon respectively at the temperature of the animal body, 38°, in water, and in the serum and blood of the horse from which carbonic anhydride had been removed as completely as possible. The results were as follows.

	Argon.	Chemical nitrogen.
In 1000 c.c. of water	25·7 c.c.	11·3 c.c.
In 1000 c.c. of blood	25·3 c.c.	11·7 c.c.

The results with serum were somewhat lower than those with blood. It follows that the solubility of argon and nitrogen in blood is practically the same as in water.

If the argon were simply dissolved from the air, the quantity in 1000 c.c. of blood would be 0·240 c.c., and it follows that, in the case of argon, as in the well-known case of nitrogen, the quantity actually dissolved in the blood is approximately double what it would be if simple dissolution took place. The hypothesis of the formation of an unstable compound of argon and some constituent in the blood is untenable, and this may also be said of the similar hypothesis that has been advanced in the case of nitrogen. The authors suggest that the membrane that separates the blood from the air in the lungs may be the active agent in causing the dissolution of abnormal quantities of the gases. C. H. B.

Estimation of Lipase. By MAURICE HANRIOT and L. CAMUS (*Compt. rend.*, 1897, **124**, 235—237).—The activity of the lipase (this vol. ii, 149) contained in the blood of the horse (collected aseptically and preserved in sealed vessels) remains constant for many months at the ordinary temperature.

Lipase (or its fermentative activity) is best estimated by the quantity of monobutyrin that it will hydrolyse in a given time. Direct experiments show that the reaction is not influenced by the presence of sodium butyrate or glycerol in much larger quantities than could result from the reaction itself. Monobutyrin, however, has a slight influence, but this is eliminated by always using solutions of the same strength.

The activity of the lipase increases with the temperature up to about 55°, but ceases almost entirely at about 60°, and entirely at 72°. When the time of action is short, the amount of change is proportional to the quantity of serum (or lipase), but if the temperature and the time are increased this proportionality no longer holds good, and the amount of change tends towards a limit which is independent of the quantity of serum added.

The activity of the lipase may be expressed in millionths of a gram-molecule of butyric acid liberated in 20 minutes at 25°. Ten c.c. of a solution of monobutyrin (1 in 100) is mixed with 1 c.c. of the serum made neutral to phenolphthalein by means of sodium carbonate, kept at 25° for 20 minutes, and the liberated acid titrated with very dilute sodium carbonate solution, using phenolphthalein as indicator. The strength of the carbonate solution may conveniently be such that each drop neutralises 0·000001 of a gram-molecule of acid. C. H. B.

[Amount of Iron Excreted in Healthy Human Urine.] By Adolf Jolles (*Zeit. anal. Chem.*, 1897, **36**, 149—158. See this vol., ii, 286).

Chemistry of Vegetable Physiology and Agriculture.

Vegetable Lipase in Penicillium Glaucum. By ERNEST GÉRARD (*Compt. rend.*, 1897, **124**, 370—371).—The ferments extracted from *penicillium glaucum* are capable of hydrolysing monobutyrin and therefore contain Hanriot's *lipase* or an analogous ferment. If the *penicillium* is cultivated on Raulin's fluid to which monobutyrin has been added, butyric acid is liberated. Emulsin, which is known to exist amongst the ferments from the *Penicillium*, does not hydrolyse monobutyrin. C. H. B.

A Soluble Oxidising Ferment and the "Breaking" of Wines. By PAUL CAZENEUVE (*Compt. rend.*, 1897, **124**, 406—408).—The "breaking" of wines is characterised by the rapid oxidation and precipitation of the red colouring matter on exposure to air, and it has frequently been attributed to the action of a soluble oxidising ferment, which, however, has never been isolated. If wine subject to this disease is treated with strong alcohol and the precipitate is purified by repeated reprecipitation with strong alcohol, a white substance is obtained which has all the properties of an oxydase; it may or may not be identical with laccase, and the author provisionally calls it *œnoxydase*. It acts on wine even below 0°, and is rapily destroyed at 65°, and instantaneously between 70° and 75°. With guaiacum, phenols, &c., it behaves in the same way as laccase. Sodium salicylate and calcium naphthosulphonate have little effect on the action of the ferment on wines, but sulphurous anhydride in quantities of 0·01 to 0·08 gram per litre, according to the richness of the wine in oxydase, are completely effective in checking the action of the ferment and preventing the breaking of the wine, as Bouffard found in 1894.

The author considers that the excessive quantity of œnoxydase in

the wines of Beaujolais in 1896 was due to special conditions of vegetation rather than to the presence of cryptogamic parasites.

C. H. B.

The Formation of Mannan in Amorphophallus Konjak. By MICHITO TSUKAMOTO (*Bull. Coll. Agric. Imp. Univ. Tokyo*, 1897, 2, 406—408. Compare Tsuji, Abstr., 1896, ii, 44, and Kinoshita, *ibid.*, ii, 60)—The leaves of this plant were found to contain very little starch, but in all parts of the leaves a very slimy substance (an anhydride of mannose) was observed. This, when boiled, loses its slimy character, and separates in a flocculent form; it agrees in all essential properties with Kinoshita's soluble mannan (*loc. cit.*). Neither pentosans nor galactans were found in the stalks and leaves.

In order to ascertain whether mannose, as such, is present in the stalk and blade, these were extracted with 50 per cent. alcohol, which would dissolve the sugar, but not the mannans. Only the extract from the stalk yielded any appreciable quantity of precipitate with phenylhydrazine acetate; in the case of the extract of the blade, there was a doubtful trace. The stalk seems also to contain glucose or fructose, or both.

The fact that the slimy mannan occurs in the leaf cells makes it probable that, to some extent, it has the *rôle* of starch in this plant; but it is at present impossible to say whether mannose is the first product of assimilation. The presence of mannose as such in the stalks is of great interest, as it has not before been observed in plants.

N. H. J. M.

Physiological Observations on Lecithin. By T. HANAI (*Bull. Coll. Agric. Imp. Univ. Tokyo*, 1897, 2, 503—506).—Maxwell (*Chem. Centr.*, 1891, i, 365) showed that the amount of lecithin increases during germination, and subsequently decreases. (Compare Frankfurt, Abstr., 1894, ii, 113; Loew, Abstr., 1896, ii, 55; Stoklasa, *ibid.*, ii, 266; Schulze and Steiger, *Zeits. physiol. Chem.*, 13, 386; Liebermann, *Pflüg. Arch.*, 1893; Schulze, Abstr., 1895, ii, 364.

The author's experiments were made with the leaves of *Thea chinensis* and the bark of *Prunus cerasus*. The following (I) amounts of lecithin, and (II) of ethereal and alcoholic extract (per cent. in the dry substance) were found at the different dates:

	Thea chinensis (leaves).				*Prunus cerasus* (bark).		
	Old leaf. 23 Nov., 1895.	Old leaf. 26 May, 1896.	Young leaf. 1 April, 1896.	Young leaf. 26 May, 1896.	23 Oct., 1895.	5 April, 1896.	9 April, 1896.
I.	2·54	0	0·21	1·11	1·88	0·96	0·71
II.	26·18	18·19	9·44	18·67	10·53	10·97	9·52

Whilst the lecithin (and the fat) decreases in old leaves in the spring, there is a gradual increase in the young leaves. The results obtained with bark also show that lecithin is a reserve substance which is consumed in the spring (compare Kellner, Makino, and Ogasawara, Abstr., 1887, 73).

The determinations were made by Schulze's method.

N. H. J. M.

Relative Value of Asparagine as a Nutrient for Phænogams. By T. NAKAMURA (*Bull. Coll. Agric. Imp. Univ. Tokyo*, 1897, 2,

465—467).—The results of experiments in which barley and onion plants were grown in solutions of asparagine and ammonium succinate respectively showed a far greater increased growth with asparagine than with ammonium succinate. N. H. J. M.

Relative Value of Asparagine as a Nutrient for Fungi. By T. NAKAMURA (*Bull. Coll. Agric. Imp. Univ. Tokyo*, 1897, **2**, 468—470). —Spores of *Aspergillus orizæ* were suspended in water, and 1 c.c. added to each of a number of flasks containing 500 c.c. of water and (except the last) 3·06 grams of ethylic alcohol, together with different ammonium salts and asparagine respectively. After 18 days, the following amounts of fungus (dried at 100°) were obtained. The amounts of salts given and of produce are in grams.

	Ammonium tartrate (6·33).	Ammonium malate (5·00).	Ammonium succinate (5·00).	Ammonium lactate (5·13).	Ammonium acetate (5·13).	Ammonium nitrate (2·66).	Asparagine (5.00).	(5·00).
Dry fungus	0·015	0·011	0·008	0·006	0·000	0·002	0·026	0·016

The solutions contained in addition monopotassium phosphate (0·1), and magnesium sulphate (0·2 per cent.).

In a second experiment, 1 per cent. methylic alcohol was added to all the flasks (except the last), and the nitrogen compounds were added in such quantities that the ratio of nitrogen atoms to carbon atoms was as 1 : 8. The following amounts of fungus were produced in 200 c.c. of the solutions.

Ammonium tartrate.	Ammonium chloride.	Sodium nitrate.	Urea.	Glycocine.	Asparagine (with alcohol).	Asparagine alone.
0·012	0·025	0·015	0·028	0·063	0·073	0·047

In mycelium fungi, asparagine is more suitable as a source of nitrogen than any other of the compounds which were used, and far more so than such a nearly related compound as ammonium succinate. The same holds good also for phænogams. N. H. J. M.

Physiological Behaviour of Maleic and Fumaric Acids. By T. ISHIZUKA (*Bull. Coll. Agric. Imp. Univ. Tokyo*, 1897, **2**, 484—486). —According to Buchner (Abstr., 1892, 820), mould fungi readily utilise fumaric acid as a source of carbon, but not maleic acid, whilst Loew (*Centr. Bact.*, **12**, 361), showed that the same holds good for bacteria. Fodera (*Chem. Zeit.*, Dec., 1895) found that maleic acid is more poisonous for the higher animals, dogs, for instance, than its stereoisomeride. Very dilute solutions of the sodium salts of the two acids were without injurious action on plants ; it is, however, possible that maleic acid is transformed in the plant into fumaric acid. The former is never found in plants, whilst the latter is known to occur (for instance, in *Fumaria officinalis*, *Corydalis bulbosa*, *Glaucium luteum*, in varieties of *Agaricus*, and in *Cetraria islandica*).

Young leaves of *Prunus cerasus* and *Brassica campestris* were killed in 4 and 3 days by 1 per cent. sodium maleate, in 6 and 5 days by sodium fumarate. Barley plants were killed in 20 hours in 2 per cent. maleate, but remained uninjured in the fumarate. In a number of experiments with branches, in 1 per cent. solutions of the sodium salts, the branches in every case lived longer in the fumarate than in the maleate. Similar results were obtained with seeds of barley and radish, and with filaments of *Spirogyra*.

Infusoria, rotatoria, and copepoda remained alive several days in 1

per cent. solutions, but were killed in 5 per cent. solutions—in 80 minutes in maleate, in 8 hours in the fumarate solutions.

N. H. J. M.

Formation of Asparagine in Plants under Different Conditions. By U. Suzuki (*Bull. Coll. Agric. Imp. Univ. Tokyo*, 1897, 2, 409—457).—According to Loew's theory, asparagine is a synthetical product, formed from the ammonia of the decomposed proteids (*The Energy of Living Protoplasm*, London, 1896, p. 38); and Kinoshita's experiments with two kinds of *Gramineæ* show that ammonia taken up by the roots may furnish asparagine.

The author has made over twenty sets of experiments, in which the different plants were placed in solutions of various ammonium salts, sodium nitrate, and urea, sometimes also with the addition of sugar; the experiments lasted for a week or more. The asparagine nitrogen was determined in similar plants, at the beginning of the experiments, in the plants fed with the various solutions, and in control plants kept in distilled water. Total nitrogen, and nitrogen as nitrates and as ammonia, were also determined in some cases. The plants selected were: sun-flower, yellow lupins, *Melia Japonica*, *Curcubita melo peppo*, potato plants and shoots, *Holesia hispidum*, buckwheat, varieties of *Brassica campestris*, wheat, and barley. The results point to the following conclusions.

Asparagine is derived, (1), from the decomposition of proteids and, (2), by synthesis from ammonium salts, urea, and nitrates. It is formed, not only by keeping full-grown plants in darkness, but also, under certain conditions, in full daylight. Synthetical formation is only possible in presence of sugar and, at the same time, under conditions which exclude the production of proteids. An excess of sugar prevents asparagine formation from proteids, but not its synthetical production.

Ammonia is never stored up in plants, being at once transformed into innocuous compounds, unless there is a deficiency of sugar present; in this case, a small amount remains in the plant. Direct experiments made by Aoyama showed the poisonous effect of ammonium salts when there was insufficient sugar to convert them into asparagine. Ammonium salts are generally more suitable than sodium nitrate for producing asparagine. The chloride is the best salt, whilst the phosphate is less suitable, owing probably to the stimulating action of the phosphoric acid in forming nuclein and new cells.

Urea proved, except in the case of barley, to be more suitable than ammonium salts for producing asparagine.

As regards nitrates, a high temperature and the presence of sugar are necessary for their conversion into asparagine; otherwise, they remain for some time stored up in the plant.

The conversion of asparagine into proteids is only possible when all conditions (the presence of sulphates, for instance) are fulfilled.

In etiolated shoots sodium nitrate is not converted into asparagine, whilst urea is. The addition of sugar increases the amount of asparagine formed from ammonium salts in etiolated plants. N. H. J. M.

Can Old Leaves produce Asparagine by Starvation? By T. Miyachi (*Bull. Coll. Agric. Imp. Univ. Tokyo*, 1897, 2, 458—464).—

A number of old leaves of *Pœonia albiflora* which showed incipient decay were divided into two portions, the one dried and analysed at once, the other placed in a vessel containing a little water. Microscopical examination revealed a gradual disappearance of starch granules from the mesophyll, and also a gradual decrease of the active albumin stored up in the vacuoles (*Bull.*, 224). After 14 days, the reserved leaves were analysed.

Experiments were also made with old leaves of *Thea chinensis*. The reserved leaves remained on the small branches, which were kept in the dark, in fresh water, for 24 days. The gradual disappearance of starch granules and the decrease of active albumin were again observed; soluble, passive albumin was not present at all. The following percentage amounts of nitrogen were found in the fresh and starved leaves.

		Total.	As Protein.	As Asparagine.	As other Amides.	As Caffeine.
Pœonia albiflora	Fresh	1·364	1·312	0·037	0·015	—
	Starved	1·462	0·801	0·206	0·455	—
Thea chinensis	Fresh	3·475	2·850	0·201	0·141	0·283
	Starved	3·987	2·511	0·867	0·251	0·358

The results leave no doubt that even old leaves can produce asparagine from proteids.

As regards the suitability of caffeine as a source of nitrogen, a 0·5 solution infected with spores of *Aspergillus orizœ* developed only a very small amount of mycelium covered with some spores, whilst *Penicillium glaucum* failed to develop at all. In the case of tea, the experiments show that, not only is there no consumption of caffeine in starved leaves, but that the caffeine actually increased. It remains to be seen whether, in presence of much carbohydrate and absence of other source of nitrogen, caffeine can be utilised for producing proteids in tea leaves.

N. H. J. M.

Tabasheer. By WALTER H. INCE (*Pharm. J. Trans.*, 1896, [iv], 2, 141).—Tabasheer is the name given to a white, smooth, porcelain-like substance rarely found deposited in a thin layer in the knots of the bamboo. The author's analyses of three samples show: SiO_2, 89·77—91·69; Fe_2O_3, trace—0·665; CaO, 0·725—3·81; K_2O, 1·524—4·332; organic matter, 0·0—3·122; water, 1·613—4·13.

R. R.

New Kino from Myristica. By EDUARD SCHAER (*Pharm. J. Trans.*, [iv], 3, 117—118).—The dried juices from the bark of several Asiatic species of *Myristica* show but little difference from officinal Malabar kino. The crude, inspissated, fresh juice from the *Myristica* species differs by containing crystalline calcium tartrate suspended in, and depositing from, it. This distinguishes it from all the other kinos of commerce.

R. R.

Brazilian and Columbian Ipecacuanha. By BENJAMIN H. PAUL and ALFRED J. COWNLEY (*Pharm. J. Trans.*, [iv], 2, 321).—By reason of the different proportions of emetine and cephæline contained in the alkaloids extracted from Brazilian and Columbian ipecacuanha, these

drugs cannot be used in medicine as equally applicable, for whilst emetine has been found better than cephæline as an expectorant, the latter is superior as an emetic. The authors have, by methods already published, separated the bases in the ipecacuanha alkaloid from each kind, with the following results per 100 parts of each total alkaloid :—

	Brazilian. Root.	Brazilian. Stem.	Columbian.
Emetine	72·14	65·6	40·5
Cephæline	25·87	32·8	56·8
Third Base	1·99	1·6	2·7

R. R.

Physiological Action of Amidosulphonic Acid. By N. MAENO (*Bull. Coll. Agric. Imp. Univ. Tokyo*, 1897, **2**, 487—493).—Plants of barley, *Brassica rapa*, *Allium fistulosum*, and soja bean were kept for some days in 0·1 and 0·05 per cent. amidosulphonic acid (as calcium salt). The plants all died after from 1 to 4 weeks. Branches of *Prunus domesticus* and leaves of *Æsculus turbinata* and of *Prunus cerasus* were also killed in a short time, similar branches and leaves remaining healthy in distilled water and in solutions of ammonium sulphate. The germinating power of seeds of rice, barley, soja bean, and turnips was also destroyed by dilute solutions of calcium amidosulphonate, but in different degrees, owing, perhaps, to the calcium salt penetrating into some more readily than into others.

The growth and fermentative power of yeast is not destroyed by amidosulphonic acid, but as a source of nitrogen the sulphonic acid is less favourable than ammonium sulphate.

As regards mammalia, the subcutaneous injection of 0·5 c.c. of 1 per cent. sodium amidosulphonate, into a white mouse, had no effect; on injecting a further 1 c.c., respiratory activity was considerably increased, but after 2 days the mouse was again in a normal condition. A mouse fed with bread soaked in the solution died; the amount of sulphonate consumed may, however, have been large. Loew found that lower aquatic animals remained alive in a 1 per cent. solution of the calcium salt. The sulphonic acid is less injurious to animals than the related carbamic acid (comp. Leo Errera, *Sur le mecanisme du sommeil*, Brussels, 1895).

Amidosulphonic acid is therefore exceptional as a poison, being poisonous neither to higher nor to lower animals, nor to fungi and algæ, whilst it destroys all kinds of phænogams. N. H. J. M.

Action of Zinc on Red Wines. By L. A. LEVAT (*Compt. rend.*, 1897, **124**, 242—243).—Zinc acts on red wines, destroying their bouquet and making them poisonous, without affecting the proportion of alcohol present. This metal should therefore not be used for the construction of receptacles, pipes, taps, &c., with which red wines are to come into contact. C. H. B.

Cause of Increased Growth of Trees when Thinned. By R. HORNBERGER (*Bied. Centr.*, 1896, **25**, 821—825; from *Forstl.-Naturwiss. Zeit.*, 1895, *Heft.* 11, 1—16).—If the increased growth of trees when thinned is due to the effect of light on the soil, resulting in the more rapid decomposition of the humus, rather than to the direct action of the light on the crowns of the trees, the wood of trees which have been thinned should be richer in ash constituents and nitrogen than that of trees which have not been thinned. It has frequently been shown that the outer wood is richer in minerals than the inner wood. The author now compares the composition of (1) the outer, (2) the intermediate, and (3) the inner wood of two beech trees over 100 years old, one of which (A) had, for 13 years, the advantage of increased light, the other (B) not. The numbers show the average results per thousand in the dry wood:

			K_2O.	CaO.	MgO.	Mn_2O_3.	P_2O_5.	SO_3.	Total.
A	Inner	wood	2·25	1·23	0·33	0·24	0·38	0·15	4·58
	Intermediate	„	1·94	1·50	0·47	0·33	0·24	0·21	4·69
	Outer	„	1·51	1·59	0·48	0·33	0·28	0·20	4·39
B	Inner	„	1·09	1·28	0·46	0·24	0·23	0·15	3·45
	Intermediate	„	2·33	1·08	0·35	0·17	0·42	—	4·35
	Outer	„	1·35	0·84	0·21	0·15	0·27	0·23	3·05

The results are opposed to those of Ebermayer, Weber, Schröder, Daube, and others, according to which the minerals decrease from the outside towards the centre. In both trees, the total ash is less in the outer than in the inner wood, and is greatest in the intermediate wood.

Comparing the outer wood of the two trees, there is a greater amount of each constituent, except phosphoric and sulphuric acids, in (A) than in (B). When the amounts of ash constituents of the outer wood are divided by the corresponding arithmetical means of those of the intermediate and inner wood, the quotients for (A), except in the case of potash, are greater than in (B). The difference is still more distinct if the outer and intermediate wood alone are considered. Under the influence of increased light, there was thus a greater percentage of mineral matter in the wood, notwithstanding that the production of wood was increased. There was also an increase in the amount of nitrogenous matter.

The results indicate that the increased production probably depended on an increased amount of available nutritive matter in the soil and increased activity of root fungi.

N. H. J. M.

Analytical Chemistry.

Gas Analysis Apparatus. By OTTO BLEIER (*Ber.*, 1897, **30**, 697—701).—A form of apparatus is described in which all the pipettes are permanently fixed to the measuring cylinder, communication being brought about by means of a many-way glass tap fixed at the head of the cylinder.

A new form of explosion pipette is also introduced, the essential feature being that the gas to be exploded is passed in a slow stream through a capillary tube, an expansion in the middle of which contains platinum wires for the passage of sparks or a platinum spiral which can be heated by an electric current. A modified form of this which admits of the introduction of potash solution is of service in the estimation of nitrogen in presence of argon, the gases mixed with oxygen being passed through the apparatus. J. F. T.

New Glass for Collecting Sediments. By EDUARD SPAETH (*Zeit. angw. Chem.*, 1897, 10—11).—This consists of an ordinary conical glass, provided at its lower end with a stopcock of peculiar construction. The glass is filled, say, with turbid water, and the deposit gradually collects in a hollow U-shaped space in the plug of the stopcock. By turning the latter in the proper direction, the water in the glass is cut off and may be thrown away. The stopcock can then be removed and the sediment subjected to microscopical examination. L. DE K.

Estimation of Fluorine in Wines or Waters. By QUIRINO SESTINI (*L'Orosi*, 1896, **19**, 253—258).—Carnot's method of determining fluorine (Abstr., 1892, 911), although somewhat long, gives results only about 1 per cent. less than that of Fresenius, but the method of Nivière and Hubert (*Mon. Scient.*, 1895, 324) gives very low results. The author has therefore devised the following rapid method of determining fluorine in wine: 100—200 c.c. of the wine is rendered slightly alkaline with sodium carbonate, and whilst boiling 2—4 c.c. of concentrated calcium chloride solution is added; the precipitate containing the calcium fluoride is ignited, mixed with precipitated silica, and placed in a U-tube about 12 inches high, which is fitted with side tubes. One arm, A, of the tube is provided with a dropping funnel, whilst the other arm has a large bulb blown on it near the top and is fitted with a thermometer; this arm is connected by the side tube with a smaller U-tube constricted at the bend, in which is placed recently filtered mercury, and, in the arm furthest from A, concentrated potassium fluoride solution. Whilst a current of dry air free from carbonic anhydride is passing through the apparatus from A, 20—30 c.c. of pure concentrated sulphuric acid is run in and the temperature gradually raised to 160°.

The air current carries the silicic fluoride into the second U-tube, and it is precipitated there as potassium silicofluoride by the fluoride solution; the latter, after half an hour's working, is poured out and diluted with an equal volume of 96 per cent. alcohol. The precipitate is collected after a few hours, washed with 60 per cent. alcohol, dried on a tared filter at 110°, and weighed. The method gives excellent results, and may also be used in the analysis of mineral waters.

W. J. P.

Toxicological Examination for Free Ammonia. By DISCORIDE VITALI (*L'Orosi*, 1896, **19**, 403—404).—In the toxicological examination for free ammonia, the author distils the solid and liquid material from a retort below 100°. The distillate, which contains the free ammonia, together with the carbonate and sulphide, is treated with

calcium chloride, and small quantities of lead carbonate are slowly added until the liquid ceases to become brown. After filtration, the liquid is again distilled, when the distillate contains only the free ammonia. W. J. P.

Volumetric Estimation of Phosphoric and Arsenic Acids. By A. C. Christensen (*Zeit. anal. Chem.*, 1897, **36**, 81—96).—The author has succeeded in applying the iodimetric method to the estimation of both free and combined phosphoric acid, and has thus developed a volumetric method which vies with the gravimetric in accuracy. Free phosphoric acid, added to a mixture of potassium iodate and iodide, liberates iodine but slowly, and to a somewhat indefinite amount. When, however, bromate is substituted for iodate, the following reaction occurs with certainty: $KBrO_3 + 6KI, + 6H_3PO_4 = 6KH_2PO_4 + 3I_2 + KBr + 3H_2O$. At ordinary temperatures, the action requires 24 hours, but at 40—50° it is complete in half an hour. For accurate results, the following conditions must be observed. The thiosulphate should be standardised against N/10 sulphuric acid, under conditions resembling those of a phosphoric acid estimation. Not more phosphoric acid should be taken than will correspond with 40 c.c. of N/10 thiosulphate. Not less than 0·5 gram of bromate and 3 grams of potassium iodide must be used, and the volume must be kept between 100 and 120 c.c. To estimate combined phosphoric acid, it is necessary to convert it into a normal alkali phosphate. When analysing calcium phosphates, this may be done by precipitating the phosphoric acid as silver phosphate, which is then decomposed by a small excess of sodium chloride. The phosphate (previously ignited, since organic matter is prejudicial) is dissolved in nitric acid and treated with an excess of silver nitrate, avoiding too great dilution. To the warm mixture, soda solution is then added until a permanent precipitate is formed, but avoiding precipitation of brown silver oxide. A 10 per cent. solution of ammonia is then dropped in until the precipitate ceases to augment and the liquid has become alkaline. The mixture is then boiled for 5—10 minutes. After allowing it to deposit, the precipitate is collected on a small filter, and washed with a 2—3 per cent. solution of potassium nitrate until free from calcium. The filter and contents are returned to the precipitation flask, and treated with sodium chloride. The solution is filtered into a stoppered bottle, and the silver chloride washed with the potassium nitrate solution until the washings are no longer alkaline. There is then added 50 c.c. of N/10 sulphuric acid and the treatment with bromate and iodide proceeded with as above. Since the reaction of sulphuric acid with the normal phosphate liberates a tribasic acid, which, however, with the bromate and iodide, reacts as a monobasic one, it follows that the difference between the c.c. of N/10 sulphuric acid taken and of N/10 thiosulphate required gives, when multiplied into 0·0049 (the half-milligram molecule of H_3PO_4), the amount of phosphoric acid present.

In presence of iron, the silver method is inapplicable. The phosphoric acid must in that case be precipitated as ammonium magnesium phosphate, and this, after washing first with ammonia and then with

90 per cent. alcohol to displace the free ammonia, is rinsed from the filter into the stoppered bottle and dissolved in the measured quantity of N/10 sulphuric acid. Equally good results were obtained, whether the precipitation by magnesia was preceded by the molybdate method or the citrate process was adopted for preparing the magnesium precipitate directly.

A precisely similar method is applicable to arsenic acid, but with results of somewhat inferior accuracy, especially when using the silver process. When, however, the arsenic acid is first converted into ammonium magnesium arsenate, and Puller's correction for the solubility of this salt in the ammoniacal wash water (1 milligram per 30 c.c.) is applied, the results agree well with theory. M. J. S.

Estimation of Pyrophosphoric Acid. By MARCELLIN P. E. BERTHELOT and GUSTAVE ANDRÉ (*Compt. rend.*, 1897, **124**, 261—265).—The precipitate formed by the action of magnesia mixture on solutions of pyrophosphoric acid in presence of acetic acid (this vol., ii, 158) has the composition $Mg_3(NH_4)_2(P_2O_7)_2 + nH_2O$, about one-quarter of the ammonium being, however, displaced by sodium. The ammonium in the precipitate has no recognisable tension of dissociation, and is not expelled when the precipitate is dried in a vacuum or when it is heated at 110°. If the precipitate is subjected to prolonged washing with dilute acetic acid, it is partially decomposed, magnesium being eliminated more rapidly than phosphoric acid. The presence of a large proportion of ammonium salts in the liquid in which the precipitate is formed is essential, otherwise the ratio of magnesium to phosphoric acid alters, and precipitation of the latter is less complete.

It is noteworthy that sodium metaphosphate, whether prepared at a high or low temperature, yields exactly the same precipitate as the pyrophosphate under the same conditions, a result due to the readiness with which the metaphosphate is converted into pyrophosphate.

C. H. B.

Volumetric Estimation of Boric Acid. By GUNNER JÖRGENSEN (*Zeit. angw. Chem.*, 1897, 5—7).—Hönig and Spitz having doubted the accuracy of the author's process (Abstr., 1896, ii, 449), he once more gives full details of the method. To estimate boric acid in milk, 100 c.c. of the sample is evaporated with a small quantity of sodium carbonate, the residue charred, and the carbon burned off as far as possible; the ash is digested for some time in dilute sulphuric acid to expel any carbonic anhydride, and the liquid, filtered from any undissolved charcoal and after adding phenolphthalein, is carefully neutralised with soda solution so as to precipitate the phosphates of the alkaline earths. To this liquid, which should not exceed 50 c.c., 20 c.c. of glycerol is added, and then standard soda, checked against boric acid, is run in until the solution becomes pink. The results are accurate, but if only very small quantities of boric acid are likely to be present, it should first be carefully tested for qualitatively. L. DE K.

Estimation of Boric Acid by Gooch's Method, and Analyses of Colemanite and Pandermite [Priceite]. By KARL KRAUT (*Zeit. anal. Chem.*, 1897, **36**, 165—167).—In consequence of the want of agreement

amongst analysts as to the trustworthiness of this method (Abstr., 1887, 299), the author gives the details of his mode of performing it, together with the results obtained in the analyses of the above native borates.

About 2—2·5 grams of lime is ignited to constant weight in a platinum crucible. The greater part is shaken out into a flask of 200 c.c. capacity, and made into a milk with water. A second flask, of the pattern used for Kjeldahl nitrogen estimations, receives the weighed borate, and is then fitted with a stopcock funnel, whilst its delivery tube dips into the milk of lime. The lime flask is kept cold. A suitable quantity of nitric acid is first introduced and distilled over, by the heat of an oil bath, then 6—8 successive quantities of methylic alcohol of 10 c.c. each, interposing at intervals the addition and distillation of 1 c.c. of water. The contents of the receiver are evaporated in a platinum basin on the water bath at the lowest possible temperature, and returned to the original platinum crucible, using nitric acid for rinsing the vessels, and then, by exposure to a gradually increasing temperature, dried and ignited, finally in a Hempel's furnace, until the weight remains constant.

Colemanite, analysed by this process, the calcium being estimated after expelling the boric acid, and the water by ignition under a layer of lime, gave numbers closely agreeing with the formula $2CaO,3B_2O_3,5H_2O$; whilst pandermite [priceite] (the specimen of which was free from sulphuric acid, barium, strontium, and magnesium) gave $4CaO,5B_2O_3,7H_2O$.

M. J. S.

Elementary Analysis in the Berthelot Calorimetric Bomb. By K. Kroeker (*Ber.*, 1897, **30**, 605—607).—In order to obtain useful results as to the heating effect of fuels by means of the calorimetric bomb, it is necessary to determine the amount of water formed by the combustion. This may be readily done, and with sufficient accuracy, by providing the bomb with two passages through the top by means of which a current of air can be passed through the instrument at the close of a combustion, and the water which has been formed weighed in the usual manner. Experiments made with pure sugar show that this can be done even in the presence of such amounts of sulphuric acid as might be formed by the combustion of coal. A. H.

Simplification of Schweitzer and Lungwitz's Method of Estimating Potassium. By Adolf Mayer (*Zeit. anal. Chem.*, 1897, **36**, 159—163).—The estimation of potassium in such substances as fertilisers, which contain sulphates, phosphates, iron, alkaline earths, &c., has hitherto required a somewhat complicated procedure for removing these impurities before the treatment with platinic chloride could be applied. Schweitzer and Lungwitz have sought to simplify this purification, by treating the solution of the original substance with a solution of barium oxalate in hydrochloric acid in sufficient quantity to precipitate all the sulphates, and then, after oxidation of the iron by hydrogen peroxide, adding an excess of ammonia, by which means the alkaline earths originally present, as well as the excess of barium added, are removed as oxalates, whilst the heavier metals are precipitated as hydroxides. A single filtration, therefore, gives a solution which only requires the expulsion of the ammoniacal salts.

Schweitzer and Lungwitz recognised that the hydrochloric acid solution of barium oxalate might be replaced by a mixture of barium chloride and oxalic acid, but they deprecated this substitution on the ground that the exact equivalence of the barium and oxalic acid ought to be ensured. The author points out that this exactitude is needless, provided care is taken that enough oxalic acid is present to precipitate all the bases. In place, therefore, of Schweitzer and Lungwitz's solution, he adds first a sufficient volume of normal barium chloride solution, and then an equal volume of normal oxalic acid, and thus overcomes one of the objections to the original process, namely, that the sparing solubility of barium oxalate in hydrochloric acid entailed the use of large volumes of reagent and a corresponding amount of evaporation. An objection to all forms of this process is, however, that, after adding the barium oxalate, the mixture must be boiled for fully 20 minutes. The time and attention which this requires constitute a substantial set-off against the simplification in other directions. M. J. S.

Estimation of Caustic Alkalis in the Presence of Alkali Carbonates. By GEORG LUNGE (*Zeit. angw. Chem.*, 1897, 41—42).—The author recommends titrating with standard hydrochloric acid, using methyl-orange as indicator, which gives the total alkali present, the carbonic anhydride being estimated in another portion of the liquid by means of the apparatus devised by Lunge and Marchlewski. When dealing, however, with a mixture containing comparatively little carbonate, the titration may be effected with sufficient accuracy by the well known method of titrating with methyl-orange and also with phenolphthalein; in presence of larger quantities of carbonates, however, the barium chloride method as devised by Winkler is preferable.

L. DE K.

Delicate Test for Copper. By A. JAWOROWSKY (*L'Orosi*, 1896, **19**, 195—196).—On adding excess of ammonia and 1 or 2 drops of phenol to a liquid (5 c.c.) containing traces of copper and agitating, it slowly becomes turbid and blue; the coloration becomes more intense on standing for upwards of an hour. On shaking with ether, the liquid clears but preserves its colour, and the precipitate collects at the boundary between the two liquids; no other metal of the fifth group gives this reaction. W. J. P.

Detection of Copper in Vegetable Substances. By BENJAMIN H. PAUL and ALFRED J. COWNLEY (*Pharm. J. Trans.*, [iv], 2, 441—442). —About 100 grams of the material is carbonised in platinum, the ash extracted with strong hydrochloric acid filtered, and the filtrate and washings of the ash collected in a porcelain dish. The insoluble residue is then treated with a few drops of strong nitric acid, dried, and ignited, the ignited mass being digested with strong hydrochloric acid, filtered, and the filtrate added to the former portion. The whole is evaporated down to about 30 c.c. and placed in a weighed platinum dish in which the copper is precipitated by pure zinc, dried, and weighed. If the copper appears to be impure, it may be dissolved in a little nitric acid and estimated colorimetrically. In 10,000 parts of the following alimentary substances, the authors'

results gave the minimum and maximum quantities of copper named:—Oysters (4 samples), 1·81—3·03; cocoa (3 samples), 0·29—0·58; spirits (5 samples), 0·01—0·05; preserved peas (11 samples), 0·54—1·44.

R. R.

Estimation of Iron in Urine. By ADOLF JOLLES (*Zeit. anal. Chem.*, 1897, **36**, 149—158).—The few investigators who have occupied themselves with this enquiry have arrived at very discordant results, in consequence, doubtless, of the errors incidental to the estimation of the very small amount normally present. Incineration being unavoidable, the following method is recommended. Five hundred c.c. of the urine, after being concentrated first on the water bath, and then in an air bath at 180° until the residue has sintered, is moistened with absolute alcohol and the alcohol set on fire. The basin is then gradually heated over a bunsen flame as long as volatile matter is given off, and the dark grey residue is rubbed to fine powder with a pestle, and transferred to a Berlin porcelain crucible, the last portions being removed by means of nitric acid; the residue is then dried and burnt to a white ash in a muffle. Platinum vessels must not be used. The ash is now completely exhausted with hot water and the insoluble residue fused with potassium anhydrosulphate. The solution is preferably reduced by zinc and titrated with permanganate, but since even the purest zinc obtainable contains traces of iron, known amounts (2 grams) must be used and the iron thus introduced allowed for. For gravimetric estimation, Gottlieb has recommended a process based on precipitation of the iron by potassium ferrocyanide, but the method, although exact, is tedious, and requires considerable analytical skill. A much more convenient precipitant is nitroso-β-naphthol, by a solution of which in 50 per cent. acetic acid the iron in a hydrochloric acid solution of urine ash is completely precipitated as pure ferric nitrosonaphthol $Fe(C_{10}H_6NO_2)_3$ (compare this vol., ii, 163). The reagent is prepared by dissolving 1·2 gram of pure crystallised nitroso-β-naphthol in 100 c.c. of 50 per cent. acetic acid at about 90°. The insoluble matter of the urine ash is heated with concentrated hydrochloric acid, which dissolves the iron completely; a small excess of the reagent is then added, the mixture stirred for 5 minutes, and, after 5 minutes' subsidence, it is filtered and the precipitate washed with 50 per cent. acetic acid until the washings are feebly yellow. The further treatment of the precipitate is not described. The urine of 12 healthy persons, examined by one or other of the above methods, side by side with Gottlieb's and Hamburger's methods (the latter a titration by permanganate after reduction by sulphurous acid) showed a total excretion ranging from 4·6 to 9·6 (average 8·0) milligrams of iron in 24 hours. Gottlieb (*Arch. für experiment. Pathol. u. Pharmakol.*, **26**, 139) found an average of 2·59 milligrams. M. J. S.

Separation of Glycerol from Wines by Means of Steam. By FRÉD. BORDAS and SIG. DE RACZKOWSKI (*Compt. rend.*, 1897, **124**, 240—242).—Fifty c.c. or 25 c.c. of the wine is placed in a flask of 300 c.c. capacity which is immersed up to the neck in a saturated solution of sodium chloride. The alcohol is completely distilled off at 110° under reduced pressure, and a slow current of steam is passed through

the liquid (still under reduced pressure) for 3 hours. The distillate is collected in two Woulff's bottles, and the rise of temperature in the receivers is sufficient to expel all the alcohol and a large part of the water, but direct experiments show that no glycerol escapes from the second bottle. The contents of the two bottles are mixed, diluted to 250 c.c. or 500 c.c., and the glycerol estimated by means of potassium dichromate as previously described (this vol., ii, 193). The results are concordant, and agree fairly well with those obtained by Pasteur's method, but are always higher. C. H. B.

Detection and Estimation of Cane-sugar in Wine. By PAUL KULISCH (*Zeit. angw. Chem.*, 1897, 45—47, 205—210).—A criticism of the conventional method adopted in Germany. The author points out that the amount of hydrochloric acid used for the inversion of the sugar is too small, as part of it is neutralised by the alkali added before the wine is submitted to distillation.

It is now proposed to use oxalic acid; 1 gram to 50 c.c. of the sample previously diluted with an equal bulk of water, or 2 grams to 50 c.c. of undiluted wine. The inversion is complete after 30 minutes' heating on the water bath. L. DE K.

Examination of Wine for Impure Starch-sugar. By LEO GRÜNHUT (*Zeit. anal. Chem.*, 1897, 36, 168—176).—The conventional methods (*Zeit. anal. Chem.*, 35) for the examination of wines containing more than 0·1 gram of total sugar in 100 c.c., involve the complete fermentation of the wine and the precipitation of the residue with alcohol (compare Abstr., 1882, 999), a procedure which, in many cases (for example, in all young wines), would prolong the analysis to an inadmissible extent. It is, however, quite easy, by a comparison of the specific rotatory power of a wine with its copper-reducing power, to select those cases where a fermentation is unavoidable. The residual unfermented sugar in natural wines being a mixture of invert-sugar and levulose, the value of $[\alpha]_D$ must lie between $-20·2°$ and $-93·3°$, and experience shows that it is uually between $-45°$ and $-90°$, and approaches the latter number the more nearly as the percentage of sugar falls. The presence of cane-sugar, maltose, isomaltose, or dextrin would reduce this lævorotation, or even convert it into a dextrorotation. If, now, the amount of a sugar is estimated by its copper-reducing power and calculated as invert-sugar, it follows, from the fact that all the above sugars, &c., reduce less copper than invert sugar, that their apparent specific rotatory power would calculate out higher than their true rotatory power. That of cane-sugar, which reduces no copper, would be $+\infty$; that of dextrin about $+3190°$. The following change in the "instructions" is therefore suggested, "If more than 0·1 gram of reducing sugar per 100 c.c. has been found, its apparent specific rotation is calculated by the formula $[\alpha]_D = \frac{100\,a}{2(c-0·1)}$ where a is the angle of rotation for sodium light by a 200 mm. column, and c the number of grams of reducing sugar in 100 c.c. Should the value for $[\alpha]_D$ thus found be positive or lie between 0 and $-45°$, the wine may contain cane-sugar, or impure starch-sugar or both. In that case, a further examination for starch sugar is to be

made." The subtraction of 0·1 from the value of *c* is made because thoroughly fermented wine still contains that amount of reducing substances, which, however, are not optically active.

As a further improvement on the official process, the author suggests the use of a minimal quantity of pure-culture wine yeast instead of the 5 grams of beer yeast specified, in order to avoid a dark colour in the concentrated syrup. M. J. S.

Sweet Wines. By WILHELM FRESENIUS (*Zeit. anal. Chem.*, 1897, **36**, 102—148).—In this important communication, the author publishes the results of the analyses of about 150 specimens of sherry, madeira, marsala, port, Cape, Malaga, Greek, Hungarian, and artificial wines, of which, in most cases, the origin was authenticated. The paper does not admit of serviceable abstraction. One of the most remarkable specimens examined was a Malaga wine (No. 19), which, although of almost unquestionable genuineness, exhibited a dextrorotatory polarisation of $+1·8°$, and presented all the analytical characteristics of a wine adulterated with starch sugar. On further examination, it yielded an unfermentable dextrorotatory constituent, which reduced more Fehling's solution after inversion than before. This is supposed to owe its origin to the boiling of the must (compare Bornträger, *Zeit. angw. Chem.*, 1892, 207). M. J. S.

Estimation of Formaldehyde. By RONALD ORCHARD (*Analyst*, 1897, **22**, 4).—The liquid containing the formaldehyde, which must be free from other reducing substances, is boiled with an ammoniacal solution of silver nitrate for 4 hours in a conical flask furnished with a reflux condenser. The precipitated metallic silver is then collected and weighed. Its weight multipled by 0·0694 represents the formaldehyde. L. DE K.

Separation and Estimation of Formaldehyde. By NORMAN LEONARD and HARRY M. SMITH (*Analyst*, 1897, **22**, 5—6). Formaldehyde, although very volatile, cannot be completely separated from its aqueous solution by distillation unless this is continued almost to dryness; for this reason, it is very difficult to recover anything like the amount added to milk.

When dealing with milk, it is best to slightly acidify with sulphuric acid before submitting it to distillation. In one experiment cited by the authors, 0·0090 gram of formaldehyde was added to 100 c.c. of milk, and 0·0056 gram was recovered from the first 60 c.c. of the distillate; the residue showed, however, a trace by Hehner's test. The estimation of the aldehyde, previously described by Smith, is based on its reducing action on potassium permanganate in alkaline solution.

When the milk is sour and decomposed, it may yield a distillate containing organic compounds, and consequently would reduce permanganate; in such cases, the process is untrustworthy. L. DE K.

Toxicological Detection of Hydrocyanic Acid. By F. FILSINGER (*Chem. Zeit.*, 1896, **20**, 305).—The author calls attention to the great delicacy of the guaiacum copper sulphate test for hydrocyanic acid.

Even when the Prussian blue and the thiocyanate test are unsatisfactory, a fine blue colour may still be obtained with the above reagent.

L. DE K.

Estimation of Stearic Acid in Fats. By OTTO HEHNER and CHARLES A. MITCHELL (*Analyst*, 1896, **21**, 316—331).—A lengthy investigation of various points concerned in this estimation containing a large amount of most valuable detail, accompanied by tables. The following process is finally recommended :—Alcohol of sp. gr. 0·8183 at 0° is saturated with pure stearic acid at 0°. From 0·5 to 1 gram of solid, or about 5 grams of liquid, fatty acids is dissolved in about 100 c.c. of the alcohol, and allowed to remain in an ice-bath overnight. The separated stearic acid is collected, washed with the cold spirit, dried, and weighed. Its melting point should not be much less than 68·5°.

L. DE K.

Estimation of Free Fatty Acids in Fats and Oils. By WM. WALTKE (*Chem. Zeit.*, 1896, **20**, 480).—The usual practice is to heat 10 grams of the sample, freed from mineral acids by treatment with hot water, with about 30 c.c. of alcohol, and to titrate with standard soda, using phenolphthalein as indicator ; 1 c.c. of normal soda equals 0·28 gram of free fatty acid. For most fats, this factor is accurate enough ; but when testing coco-nut oil, it cannot be used, as the factor depends on the molecular weights of the fatty acids, which, for this oil, vary from 205 to 240. The molecular weight of any given sample is, however, readily obtained by isolating the fatty acids and titrating a known weight of the dried acids with $n/5$ soda in alcoholic solution.

L. DE K.

Estimation of Potassium Hydrogen Tartrate in Wines. By HENRI GAUTIER (*Compt. rend.*, 1897, **124**, 298—300).—One hundred c.c. of the wine is concentrated to about 15 c.c. and allowed to remain for two or three days in a cool place at a fairly constant temperature, a flask containing a saturated aqueous solution of potassium hydrogen tartrate being placed near it. The wine residue is filtered through a small filter into a graduated measure, in order that the volume of the liquid may be ascertained. The precipitate on the filter is washed with the saturated solution of potassium hydrogen tartrate, and is then transferred to a flask, mixed with a volume of the hydrogen tartrate solution exactly equal to the volume of the filtrate from the wine residue, diluted to about 100 c.c. with water, heated gently to dissolve the salt, and titrated with potassium hydroxide solution, using phenolphthalein as indicator.

A correction is necessary, because the solubility of potassium hydrogen tartrate in water is greater than its solubility in the wine residue, and this correction is independent of the source of the wine. It amounts to 0·15 gram of potassium hydrogen tartrate per litre for every 10 c.c. of concentrated wine residue, and this must be subtracted from the quantity found by the author's method. C. H. B.

Colour Reactions of Organic Acids, principally Tartaric, Citric, and Malic. By EUGENIO PIÑERÚA (*Chem. News*, 1897, **75**, 61 ; and *Compt. rend.*, 1897, **124**, 291—292).—0·5 gram of the organic acid is

carefully heated with 10 to 15 drops of a fresh solution containing 0·02 gram of β-naphthol in 1 c.c. of sulphuric acid, sp. gr. 1·83. Tartaric acid gives at first a blue coloration changing to green, and on mixing, when cool, with 15 to 20 vols. of water, it becomes reddish-yellow. Citric acid gives a blue that does not change to green unless tartaric acid is also present; on diluting, it becomes colourless or faintly yellow. Malic acid gives at first a greenish-yellow, becoming bright yellow, and on diluting bright orange. Other organic acids give less distinct and characteristic reactions; nitrites, nitrates, and chlorates also produce colour reactions; thus sodium nitrite gives a very strong red, unchanged by dilution. A solution containing 0·1 gram of resorcinol in 1 c.c. of sulphuric acid (66°) gives a reddish-brown, becoming an intense violet on further heating, and orange on dilution; with sodium or potassium nitrate and with potassium chlorate an intense green, changing to brown on dilution. D. A. L.

Identification of Citric Acid. By LUDV. STAHRE (*Zeit. anal. Chem.*, 1897, **36**, 195; from *Nordisk Famaceutisk Tidskrift*, **2**, 141).—The test is based on the fact that citric acid, on oxidation, yields acetone, which, by the action of bromine, is converted into bromacetone. The solution to be tested is mixed with a few drops of permanganate and warmed (but not to boiling) until the red colour has disappeared. A few drops of bromine water are then added, when a white turbidity or precipitate is produced, either immediately or on cooling. As little as 0·2 milligram of citric acid in 1 c.c. still yields an opalescence. On adding soda, the well known odour of bromoform is evolved. The bromine may also be added before the permanganate, and in that case less permanganate is required. This form of the test should be used when tartaric or malic acid is present. Malic acid produces the odour of bromoform on addition of soda; tartaric acid does not.

M. J. S.

Testing Lemon Oil. By HENRY GARNETT (*Pharm. J. Trans.*, 1896, [iv], **2**, 323).—The quantitative determination of the citral in lemon oil is stated to be the most trustworthy test of its value, and the author now proposes a process for this estimation founded on the reduction of citral to geraniol, and the conversion of the latter into its acetate, which admits of saponification by a standard solution of potassium hydroxide. The reduction of the citral is effected by dissolving the lemon oil in an equal volume of glacial acetic acid, and gradually and cautiously adding metallic sodium (5 grams for 20 c.c. of oil). The cooled liquid is diluted, transferred to a separator, the oil washed free from acid, dried, boiled with acetic anhydride to convert it into its acetate, washed until neutral, dried by contact with anhydrous sodium sulphate, and the whole, or a portion, taken for hydrolysis with excess of normal alcoholic potash, the excess of alkali being then titrated. 6·49 to 7·07 per cent. of citral was found in samples of pure lemon oil. R. R.

Testing the Purity of Rose Oil. By ROBERT JEDERMANN (*Zeit. anal. Chem.*, 1897, **36**, 96—102).—The tests hitherto depended on for detecting the presence of geranium oil, namely, the sulphuric acid test and the solidifying temperature, are shown to have a very limited value.

Two forms of the sulphuric acid test are in current use. The German Pharmacopœia prescribes mixing 5 drops of the oil with 25 drops of pure concentrated sulphuric acid, and the subsequent addition of 10 c.c. of alcohol of 0·81 sp. gr. The American Pharmacopœia uses only 5 drops of sulphuric acid and 2 c.c. of alcohol. Geranium oil under these conditions gives a markedly turbid solution, whilst genuine rose oil is supposed to give a colourless and nearly clear one. An extensive experience of genuine East Roumelian rose oil shows that comparatively few specimens will pass this test. The turbidity is due to the presence of traces of resinous substances which distil over with the oil, and under some circumstances may increase markedly in amount, without, however, impairing the fineness of the article as a perfume. Equally little is a high solidifying point to be trusted as evidence of high quality. It may, indeed, indicate the absence of geranium oil, but is also compatible with the presence of an unduly large proportion of the inodorous stearoptene. In consequence of conditions obtaining during the distillation, the limits 17·5—20° usually adopted may be widely deviated from in both directions. The index of refraction is a more trustworthy indication. The average for genuine oil at 30° may be taken as 43° 30′, whilst that of geranium oil is 41° 30′. Further, at 30°, the specific gravity of rose oil varies only between 0·8555 and 0·8645, whilst that of geranium oil is 0·883—0·8895. Although a combination of the above tests may furnish presumptive evidence as to genuineness, yet a careful attention to the odour, and to the practical results obtained in the application to perfumery, are the most satisfactory guarantees of quality. M. J. S.

Essential Oils of Black and White Peppermint. By John C. Umney (*Pharm. J. Trans.*, 1896, [iv], 2, 123—125).—The oil of white peppermint may be distinguished from that of black peppermint by its greater optical activity; its not depositing menthol at a low temperature; its containing a greater proportion of menthol acetate and isovalerate, and by its giving an intense blue coloration with coppery fluorescence when it is mixed with 3 parts of glacial acetic acid and allowed to remain some hours; the black peppermint oil gives only a very pale colour. R. R.

Detection of 'Rosin Oil' in Fatty Oils. By Cornette (*L'Orosi*, 1896, 19, 234—235).—"Rosin oil" is sometimes used as an adulterant of fatty oils; its presence may be detected by saponifying 10 c.c. of the oil with soda, dissolving the soap in hot water, and adding excess of concentrated sodium chloride solution after cooling. The sodium salt of the fatty acid is thus precipitated, whilst the sodium salt derived from the rosin oil remains dissolved; the liquid is filtered, the precipitate washed with salt solution, and the rosin oil acids liberated from the clear filtrate by sulphuric acid. The acids soon solidify, and may be collected on a tared filter and weighed. W. J. P.

Rancidity of Olive Oil. By Quirino Sestini (*L'Orosi*, 1896, 19, 361—367).—From determinations of the total and free acidity of 35 samples of olive oil, the author concludes that the acidity number is no criterion of the state of rancidity of olive oil. W. J. P.

Discrimination between Boiled and Unboiled Linseed Oil. By GIULIO MORPURGO (*L'Orosi*, 1896, **19**, 373—374).—Of late years, drying oil has been prepared in England by treating with oxygen in a special apparatus linseed oil in which rosin has been dissolved ; the prepared oil is only distinguished with difficulty from the unboiled oil, as it contains no metallic oxides in solution, as in the case of ordinary drying oil. The author saponifies 20 c.c. of the oil with a slight excess of soda, then adds excess of sodium chloride to the aqueous solution, and after a time filters off the soap; the filtrate from boiled oil becomes turbid on adding acetic acid, whilst that from the unprepared oil remains nearly or quite clear. W. J. P.

The Iodine Number of Oils. By HUGO MASTBAUM (*Zeit. angw. Chem.*, 1896, 719—721).—The iodine number of an oil is always higher when the sample is a cold-pressed one. In their investigations of the iodine number of linseed oil, van Ketel and Amtusch made use of oil extracted by means of light petroleum, and consequently got an article containing more stearin than the commercial oil, and giving therefore a somewhat lower Hübl figure. L. DE K.

Estimation of Antipyrine. By CARL KIPPENBERGER (*Zeit. anal. Chem.*, 1896, **35**, 659—677).—Phenyldimethylpyrazolone, known in commerce as antipyrine, analgesine, anodynine, metozine, parodyn, phenylone, sedatine, or phenazone, is completely precipitated either from neutral or (mineral) acid solutions by iodine dissolved in potassium iodide, the product being a periodide of the composition $C_{11}H_{12}N_2O,HI,I_2$. Manseau's method of titration is based on this fact, but the conditions under which he worked did not afford correct results. Neutral solutions, or solutions acidified with hydrochloric acid, consume considerably more than the theoretical amount of iodine, but when the antipyrine is first converted into hydriodide by the addition of hydriodic acid, or when sufficient hydriodic acid is present in the iodine solution, exactly 2 atoms of iodine are consumed by 1 molecule of antipyrine. A measured quantity of the approximately 1 per cent. antipyrine solution is therefore mixed in a dry stoppered bottle with a small excess of N/20 iodine solution made with 10 grams of potassium iodide and 40 c.c. of 52 per cent. hydriodic acid (sp. gr. 1·7) in the litre. After shaking until the periodide has collected as a tarry mass of dark brown colour, and the supernatant liquid has become clear, the mixture is filtered through purified asbetos into a dry burette, and in an aliquot part the excess of iodine is titrated by N/20 thiosulphate. The results are sufficiently exact for most purposes, but in consequence of a slight solubility of the precipitate in hydriodic acid and iodide solutions, absolutely exact results can only be obtained by standardising the iodine solution against known amounts of antipyrine. Special experiments were made to ascertain whether acetanilide, phenacetin, sulphonal, aniline, or cane-sugar would disturb the results, but all were found to be without influence, especially if the solution is feebly acidified with hydrochloric acid. M. J. S.

Micro-crystallographic Detection of Alkaloids. By VADAM (*J. Pharm.*, 1896, [6], 4, 485—488).—The author makes use of the following reagents. 1. Mayer's reagent. 2. Bouchardat's reagent (dilute solution of iodine in potassium iodide). 3. Saturated solution

of picric acid. 4. Gold chloride (1 : 20). 5. Platinic chloride (1 : 20). 6. Schulze's reagent (sodium phosphantimonate). 7. Sodium phosphotungstate. 8. Cadmium iodide (1 : 10). 9. Saturated solution of potassium dichromate. 10. Do. of potassium ferrocyanide. 11. Do. of potassium ferricyanide. 12. Sodium nitroprusside (1 : 10).

The alkaloid residue obtained by any of the usual methods of extraction, is weighed and dissolved in hydrochloric acid (diluted to 1/50) in such a manner as to give an alcoholic solution of about 1/200.

A dozen object glasses are placed in a row. A drop of the alkaloidal solution is put on each, and then a drop of the various reagents is added. Cover slips are put on, and the 12 slides, after being allowed to stand for half-an-hour, are examined microscopically with a low power, and the results noted. J. J. S.

Kruger and Wulff's Method of Estimating Xanthine-bases in Urine. By KARL H. HUPPERT (*Zeit. physiol. Chem.*, 1897, **22**, 556—560).—Precipitation of xanthine bases in the urine by cuprous salts as recommended by Krüger and Wulff gives results which are too high, because other constituents of the urine are carried down as well. Haycraft's silver method is recommended. W. D. H.

Estimation of Caffeine in Tea, Coffee, &c. By A. DELACOUR (*J. Pharm.*, 1896, [6], 4, 490—491).—The author recommends the following method. Two grams of the finely divided substance is boiled with 80—90 c.c. of distilled water for some 10 minutes in a 100 c.c. flask ; when cold 4 c.c. of lead acetate solution is added, the solution made up to the mark, shaken, and then filtered. Fifty c.c. of the clear filtrate is placed in a separating funnel, 10—15 drops of acetic acid added, and the mixture extracted four times with 20—25 c.c. of chloroform, the chloroform extracts are run into a tared flask, the chloroform slowly evaporated, and the residue dried and weighed. J. J. S.

Estimation of Morphine in Opium. By GUSTAV LOOFF (*J. Pharm.*, 1896, [6], 4, 312).—The author finds that sodium salicylate readily precipitates the resinous matter contained in opium extract, and also a part of the narcotine. The morphine can then be precipitated from the clear filtrate by means of ammonia and a little ether. After stirring for some 10 minutes, a white precipitate is obtained; the small quantity of narcotine contained in this can be removed by means of benzene after the precipitate has been dried. J. J. S.

Modification of De Vrij's Chromate Process. By LEONARD DE KONINGH (*Ned. Tydschr. Pharm.*, 1897, 97—98).—The original method does not provide for the presence of cupreine sulphate in commercial quinine sulphate. The following modification is proposed. Two grams of the sample is dissolved in 80 c.c. of hot water, and mixed with 12 c.c. of a 5 per cent. solution of pure potassium chromate. When cold, the liquid is filtered, and 5 c.c. of a 10 per cent. solution of soda is added to the filtrate, when an immediate precipitate or turbidity will prove the presence of cinchonidine, quinidine, cinchonine, or hydroquinine. After filtering, the liquid is freed from traces of these alkaloids by agitating twice with ether or, better, chloroform (first 10 and then 5 c.c.)

and after adding 2 grams of ammonium chloride, it is again agitated repeatedly with chloroform, which dissolves the cupreine; this is left on evaporating the solvent, and may then be further tested. L. DE K.

Detection of Aconitine. By WYNDHAM R. DUNSTAN and FRANCIS H. CARR (*Pharm. J. Trans.*, 1896, [iv], 2, 122—123).—When a solution of an aconitine salt is mixed with a very slight excess of a solution of potassium permanganate, a purple, crystalline precipitate is produced which is fairly stable, especially in presence of a small quantity of acetic acid. In very dilute solutions, the precipitate appears after standing and stirring, as in the case of a 0·025 per cent. solution; but a 0·05 per cent. solution gives an immediate precipitate. It is possible to detect 0·000025 gram of aconitine by this means. Other alkaloids which give precipitates with the permanganate behave differently in this reaction. Cocaine salts are not distinctly precipitated in solutions containing much less than 1 per cent. of the alkaloid, and although the precipitate is crystalline, it is readily dissolved by water, as is that of hydrastine, which is not crystalline, and is pinker than the aconitine compound. The same is true of papaverine. Pseudaconitine most nearly resembles aconitine in this respect, but it is not precipitated readily in solutions containing much less than 0·5 per cent.; the precipitate dissolves when the liquid is heated, and separates out on cooling, whereas the aconitine precipitate rapidly darkens when warmed. Aconine salts are not precipitated by the permanganate, nor is a 1 per cent. solution of benzaconine acetate. R. R.

Estimation of Aconitine. By WYNDHAM R. DUNSTAN and THOMAS TICKLE (*Pharm. J. Trans.*, [iv], 2, 121).—Pure aconitine may be very accurately estimated by heating its sulphate in a closed tube with water at 125° for 3 hours, when it undergoes partial hydrolysis with production of one molecular proportion of acetic acid and the separation of a little benzoic acid. The liquid, as taken from the tube, is made alkaline with pure sodium hydroxide, and the alkaloid is removed by twice shaking with chloroform; the aqueous liquid is acidified with sulphuric acid, and the benzoic acid removed by agitation with benzene, after which it is distilled until the whole of the acetic acid has come over, when the distillate is titrated with baryta water, using phenolphthalein as the indicator. This method is, however, quite inapplicable to the total alkaloid obtained from the root of *Aconitum napellus* and the preparations from it, because certain amorphous, inseparable alkaloids which are present also yield acetic acid. From a mixture of these amorphous bases, which would probably contain less than 5 per cent. of aconitine, the acetic acid produced corresponded with 34 per cent. It follows that the galenical preparations made from *A. napellus* cannot at present be standardised. R. R.

Estimation of Total Alkaloids in Coca Leaves. By ALEXANDER GUNN (*Pharm. J. Trans.*, [iv], 3, 249—250).—The different processes that have been proposed for the estimation of the alkaloids in coca leaves were compared, and found to yield results which show great divergence. Lyons' process is considered to effect a complete extraction of the alkaloids, but requires 24 hours to carry out. Results almost identical

can be obtained in 2 hours, as follows. Five grams of the powdered leaves are moistened with weak ammonia (2 per cent.), allowed to remain half an hour, then placed in a narrow tubular percolator (10 × $\frac{1}{2}$ inch), and treated with ammoniated ether until about 100 c.c. has passed through. The ethereal liquid is shaken three times with hydrochloric acid (2 per cent.; about 50 c.c.), the acid extract washed with ether, made alkaline with ammonia, and then extracted three times with ether. The ethereal extract is collected in a weighed porcelain dish, evaporated, and dried at 75°. R. R.

Detection of Aniline-blue in Bread. By CHARLES VIOLETTE (*Bull. Soc. Chim.*, 1896, [3], **15**, 456).—A trace of aniline-blue is often employed by bakers to counteract the yellow colour of bread made from oatmeal or inferior flour. A filter paper is placed on a plate and covered with water a few millimetres deep, the suspected bread is crumbled on to the plate, and the filter paper is subsequently examined for blue spots. M. W. T.

Detection of Coal Tar Colours in White Wines, and their Distinction from Caramel Colours. By ALBERTO D'AGUIAR and W. DA SILVA (*Compt. rend.*, 1897, **124**, 408—410).—Experiments were made with white wine to which had been added small quantities of dinitronaphthol, chrysoidine, Bismarck brown, orange II, tropeolin, Biebrich scarlet, azoflavin, helianthin, methyl-orange, amidoazobenzene, naphthol-yellow S, or caramel, as the case might be. Sixty c.c. of each wine was made alkaline with ammonia, and agitated with 30 c.c. of amylic alcohol; the latter was separated, filtered, the intensity of the coloration observed, and part of the solution reduced to one-third its original volume, in contact with some threads of silk. In a second series of tests, 5 c.c. of the amylic alcohol solution was evaporated to dryness on a water bath, and the residue was treated with concentrated sulphuric acid to which water was afterwards added. Another set of similar experiments was made, using hydrochloric acid instead of sulphuric. In a third series, the residues, after being heated with concentrated sulphuric acid and water, were filtered, made alkaline with ammonia, again agitated with amylic alcohol, and the second solution thus obtained was treated in the same way as the first.

It was found that caramel scarcely gives any coloration to the amylic alcohol, whilst naphthol-yellow S, the only one of the dyes that gave doubtful results, is readily recognised in other ways. Caramel has practically no dyeing effect on silk, and whilst this is true also of chrysoidine and amidoazobenzene, the latter are readily recognised in other ways. In the tests with sulphuric acid, the results obtained with caramel are very distinct. The general conclusion is, that the amylic alcohol method is not likely to lead to any confusion between coal-tar colours and caramel. C. H. B.

Reagent for Detecting Albumin and Peptones in the Urine. By A. JAWOROWSKY (*L'Orosi*, 1896, **19**, 379).—A reagent composed of ammonium molybdate (1 part) and tartaric acid (4 parts) dissolved in water (40 parts), when added to slightly acid urine, gives a whitish precipitate in presence of albumin or peptones, which, in the former

case, is not dissolved by heat, but in the latter dissolves on heating, and separates again on cooling. Most alkaloids are precipitated by this reagent; if these are present, citric acid should be substituted for the tartaric acid used in its preparation, and the urine submitted to a preliminary treatment. This consists in adding excess of sodium carbonate, filtering, evaporating to one third, again filtering, extracting with amylic alcohol, and neutralising with citric acid. W. J. P.

Estimation of Gluten in Flour. By BALLAND (*J. Pharm.*, 1896, [6], **4**, 250—251).—When flours containing the same percentage of nitrogen are treated by the usual method, they may yield different amounts of gluten. This depends on the sifting and also on the milling process—that is, on the amount of bran which they contain. The estimation of gluten, therefore, whilst supplying a precise method for determining the quality of a flour, is inadequate for determining the amount of nitrogenous substances present, or, in other words, for determining its nutritive value. J. J. S.

Detection of Tussah in Silk Fabrics. By F. FILSINGER (*Chem. Zeit.*, 1896, **20**, 324).—After explaining the difficulty of a microscopic investigation, the author calls attention to the fact that, whilst real silk is readily soluble in hydrochloric acid, strong zinc chloride or an alkaline solution of copper-glycerol, tussah silk is scarcely affected by these solvents.

Another peculiarity is that, whilst silk is not readily combustible, tussah silk takes fire much more readily without emitting the unpleasant odour of burning silk. L. DE K.

Estimation of Lipase. By MAURICE HANRIOT and L. CAMUS (*Compt. rend.*, 1897, **124**, 235—237).—See this vol., ii, 273.

General and Physical Chemistry.

Spectro-chemistry of Nitrogen. V. By JULIUS W. BRÜHL (*Zeit. physikal. Chem.*, 1897, 22, 373—409).—The author adds to those already published, a large number of observations on the refraction and dispersion of nitrogen compounds. The solids were examined in solution, the solvents employed being ethylic alcohol, acetone, ethylic acetate, benzene, α-bromonaphthalene, ethylic ether, and carbon bisulphide. The sources and the methods of purification of the compounds are given, and the results obtained are shown in the accompanying table, (1) being the molecular refraction for the sodium line, and (2) the dispersion $M\gamma—M\alpha$, calculated according to the Lorenz formula.

Compound.	1	2
Hydrogen nitrate	10·003	0·338
Hydrazine	8·867	0·266
Methylnitramine	16·79	0·76
Isocyanogen tetrabromide	50·42	2·76
as.-Dimethylhydrazine	18·68	0·60
Dimethylnitramine	21·65	0·95
Formodimethylamide	19·86	0·65
Chloroformodimethylamide	24·88	0·77
Methylethylnitramine	25·82	1·07
Thiophen	24·33	1·08
Ethylic sulphide	28·51	0·88
Imidoethylic ether	24·35	0·64
Acetodimethylamide	24·23	0·74
tert.-Butylamine	24·20	0·64
Pyrazine	22·64	1·15
Pyridazine	22·15	0·99
Dimethylfurazan	23·98	0·66
Ethylic methylnitrocarbaminate	32·26	1·13
Butylnitramine	30·57	1·13
sec.-Butylnitramine	30·48	1·10
Methylbutylamine	28·76	0·76
Imidopropyl ethyl ether	28·76	0·75
Diethylic imido-carbonate	30·53	0·77
Methylpyrazine	27·14	1·35
Methylethylfurazan	28·57	0·77
as.-Methylbutylhydrazine	32·50	0·92
Nitropiperidine	32·93	1·26
Methylbutylnitramine	35·05	1·30
Isobutylmethylnitramine	35·14	1·31
Nitrosoethylurethane	36·33	—
Metabromonitrobenzene	40·45	2·36
Propylpropylideneamine	32·44	0·93
Methylic butylcarbamate	34·85	0·90
Methylic isobutylcarbamate	34·89	0·90
Methylic sec.-butylcarbamate	34·80	0·88
Ethylic dimethyloxamate	35·70	1·06
Propylglyoxalidine	33·42	1·06
Dimethylketazine	35·98	1·41
Methylic butylnitrocarbamate	41·39	1·35
Methylic sec.-butylnitrocarbamate	41·38	1·34
Methylic isobutylnitrocarbamate	41·38	1·34
Ethylic butylnitrocarbamate	46·08	1·45
Ethylic sec.-butylnitrocarbamate	46·08	1·45
Ethylic isobutylnitrocarbamate	46·07	1·47
Hexylnitramine	39·79	1·34
Triformalmethylamine	38·72	1·16
Furylimidoethyl ether	37·46	1·71
Ethylic butylcarbamate	39·53	0·99
Ethylic sec.-butylcarbamate	39·56	0·99
Ethylic isobutylcarbamate	39·52	1·00
γ-Coniceine	39·22	1·06

Compound.	1	2
Isocaproimidoethyl ether	42·20	1·05
Quinoxaline	40·45	3·03
Benzylmethylnitramine	45·28	2·11
Methyl ethyl ketazine	45·26	1·63
Methylmethenylphenyleneamidine	40·09	2·16
Isoquinoline	41·43	2·65
Ethylic hexylcarbamate	48·84	1·22
Toluquinoxaline	45·31	3·44
Triformalethylamine	52·44	1·50
Orthotoluquinoline	46·62	2·98
Metatoluquinoline	46·77	3·02
Paratoluquinoline	46·88	3·03
γ-Methylquinoline	46·11	2·88
α-Methylisoquinoline	46·03	2·85
Kairoline	48·02	2·58
Isoamylideneamine	51·39	1·42
Ethylethenylphenyleneamidine	49·66	2·52
Propylpropenylphenyleneamidine	59·07	2·86
Triformalpropylamine	66·30	1·80
Benzylamine acetoacetate	66·62	4·05
Solutions.		
Isocyanogen tetrabromide	50·82	2·91
Nitrourethane	27·80	1·03
Pyrazine	22·49	1·16
Methylglyoxalidine	24·43	0·84
Diethylic chlorimidocarbonate	35·88	1·01
Diethylic bromimidocarbonate	38·40	1·29
Nitrobenzene	30·01	1·17
β-Phenylhydroxylamine	32·48	1·72
Tetramethylethylene nitroso-chloride	(Hγ) 38·33	
Phenylnitramine	37·95	2·87
Parabromophenylnitramine	46·71	
Orthonitrophenylnitramine	44·04	
Metanitrophenylnitramine	44·87	
Paranitrophenylnitramine	47·36	
Paranitrodiazobenzene methyl ether	47·76	
Paranitrobenzylnitramine	48·39	3·26
α-Paranitrobenzylnitramine(-N-)-methy ether	53·09	3·41
β-Paranitrobenzylnitramine(-O-)-methy ether	53·99	3·42
Paranitrobenzylisonitramine methyl ether	53·52	2·88
α-Benzylamine acetoacetate	67·90	4·37
β-Benzylamine acetoacetate	67·78	4·37
α-Dibenzylnitrosohydroxylamine	70·77	
β-Dibenzylnitrosohydroxylamine	71·02	3·54
Benzylaminoethylic cinnamate	87·52	5·91

L. M. J.

Apparatus for Examining the Spectra of Gases. By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1897, **124**, 525—528).—The author describes an apparatus for facilitating the examination of the spectra of gases under atmospheric pressure. Although inferior to the ordinary Plucker tubes as regards definition of the lines, the simplicity of construction and ease of manipulation make it possible to include an examination of the spectrum in the ordinary qualitative analysis of a gas. The apparatus consists of a straight glass tube, 10 to 12 cm. long and 7 to 15 mm. broad, closed at one end, into which a platinum wire is fused. A second and much narrower tube is bent in the form of a V, and has a platinum wire running through its whole length, and projecting at both ends. At one end, which serves as one of the poles for the electric discharge, the glass is fused round the wire; the other end can be connected with the coil. The sealed limb of the second tube is fitted into the first tube by means of a cork, in such a way that it can slide up and down, so that the distance between the two platinum wires can be adjusted. A short capillary tube must also pass through the cork, or there must be a notch in its side to allow for the expansion due to the sparks. The straight tube is filled with mercury, placed in a small mercury trough, and a small quantity of the gas to be examined is passed into it. The bent tube is now slipped up into it, and the cork fitted into its place. A condensed or uncondensed spark is passed between the platinum wires, the distance between them being adjusted to give the best result. The discharge should be frequently interrupted, and a condensed spark should be avoided if possible. C. H. B.

Unknown Lines observed in the Spectra of certain Minerals. By J. NORMAN LOCKYER (*Proc. Roy. Soc.*, 1896, **60**, 133—140).—Photographs of the spectra, at atmospheric pressure, of the following gases, which from experience are likely to be associated with those given off by minerals, have been obtained, and the lines tabulated:—Nitrogen, oxygen, chlorine, carbonic anhydride, coal gas, sulphuric anhydride, phosphoretted hydrogen, and argon. The lines of mercury, potassium, and platinum have also been photographed, the latter because they are always present in the spectra, for the reason that the spark is passed through platinum poles, whilst the lines of mercury and potassium frequently occur, according as the gases are collected over mercury or potash.

A list of the lines obtained for the gas from eliasite is given, after eliminating the lines due to the old gases. The wave-lengths of several of the former lines approach very near those of the latter.

Attempts have been made to concentrate the eliasite gas, but the quantity is so small, and so largely admixed with helium and argon that a new research with larger amounts of material is essential.

A complete list of the unknown lines so far noticed in other minerals is also given, together with the facts as to whether or not lines nearly coincident in position have been observed in any celestial body.

A. W. C.

Spectrum of Cyanogen as Produced and Modified by Spark Discharges. By W. NOEL HARTLEY (*Proc. Roy. Soc.*, 1896, **60**, 216—221).—The chief evidence of the existence of a cyanogen spectrum

is that this substance is actually synthesised in the arc when nitrogen is present; that without nitrogen elementary carbon does not yield the same spectrum; that cyanogen gas burns with a flame of which the banded spectrum is known as that of cyanogen by reason of the foregoing facts; and, lastly, that when a condensed spark is passed between electrodes of gold in an atmosphere of cyanogen, the same spectrum can be photographed.

Facts are recorded which lend support to the view that the flame of burning cyanogen ought to exhibit the spectrum of carbon.

The author considers that the facts derived solely from observations on the arc are insufficient to establish the existence of a definite cyanogen spectrum. Moreover, it has been shown that lines somewhat resembling the edges of the cyanogen bands are seen when graphite poles are moistened with water and the spark passed through air; if the water contains the chlorides of ammonium, calcium, or zinc, the lines are intensified and develop into bands which become stronger with concentration of the solution; the explanation of this is that the only mineral acid free from ammonia is freshly made sulphurous acid. Salts of calcium or zinc prepared from ordinary mineral acids always contain ammonium salts; hence, if the bands said to be cyanogen bands are due to the nitrogen of the ammonia, the spectrum of the graphite poles will exhibit bands more strongly, as the solution used is more concentrated.

That the bands and lines are really due to cyanogen and not to elementary carbon is proved by the following facts.

The lines belonging to the edges of the bands in the spectra of a flame of cyanogen were found to coincide exactly with those photographed from a potassium cyanide solution, when the spark was passed in an atmosphere of carbonic anhydride or cyanogen; or when the spark was passed between gold electrodes in cyanogen gas.

The cyanogen spectrum in the flame of burning cyanogen is accounted for because there is excess of the gas present and the temperature of the flame is exceedingly high, but the gas within it is not in contact with a solid substance, hence immediate decomposition does not occur, and the gaseous compound is only heated to incandescence.

A. W. C.

Birotation of Glucose. By HEINRICH TREY (*Zeit. physikal. Chem.*, 1897, 22, 424—463).—The author had previously investigated the effect of acids on the birotation of aqueous and alcoholic solutions of glucose and glucose anhydride (Abstr., 1896, ii, 139), and the observations are here extended to the effect of various salts and of other solvents. Sodium sulphate and acetate, potassium nitrate and iodide, ammonium chloride and thiocyanate, barium chloride, magnesium sulphate and chloride, aluminium chloride, lead acetate, mercuric chloride, and cadmium iodide all caused in N/20 solutions an acceleration of the retrogression, that due to the magnesium salts being most marked. Sodium chloride alone of all the salts examined has a retarding influence (compare Levy, Abstr., 1895, i, 586). In methylic alcohol solution, cadmium iodide produced a marked increase, and potassium iodide a slight increase of velocity, the final value being only slightly different from that of a pure alcoholic solution. By

increasing the concentration of the salts, however, the acceleration can be changed to a retardation. The effect of alkaline solutions was investigated, and with sodium hydroxide the ordinary limit of about 50° is almost immediately obtained, but the value does not remain constant, as it further diminishes and may attain zero or even a negative value. Sodium carbonate gives a constant value of about 50° very speedily, whilst ammonia and potassium cyanide cause a further decrease below this value. The effect here appears to be due to the presence of hydroxyl ions, for the measurement of which the author considers the reaction very convenient. The accelerative effect of sulphuric acid is diminished by the addition of sodium sulphate, that of hydrochloric acid, however, being increased by the addition of sodium chloride, and also by the addition of alcohol. Acetic and propionic acids cause a decrease, cacodylic acid an increase, of velocity, and neutral compounds such as cane-sugar appear to have a slight retarding effect. Multirotation also occurs in acetone solutions, the behaviour being very similar to that of solutions in methylic and ethylic alcohols. Measurements were also made of the internal friction of aqueous and alcoholic solutions of the anhydride and hydrate, the values being slightly different for the two compounds. L. M. J.

Theory of Accumulators. By KARL ELBS (*Zeit. Elektrochem.*, 1896, **3**, 70).—The source of the electromotive force of a secondary battery is to be found, according to Le Blanc, in the change of quadrivalent into bivalent lead ions; whereas, Liebenoff and Löb assume the presence of the ion $\overset{--}{PbO_2}$ in the solution, which, on abandoning its charge, is deposited as lead peroxide. The author is led, by his observations on the electrolysis of solutions of the acetates, to support the first view. The acetates are divided into three groups: (1) Those yielding, at the anode, mainly ethane and carbonic anhydride; (2) those yielding mainly oxygen; (3) those from which no gas is evolved. Group (1) includes the acetates of metals of constant valency; group (2) contains the acetates of metals which are bi- or trivalent, and whose higher oxide yields less stable salts than the lower; group (3) contains metals of valency between two and four which form comparatively stable peroxides. In the last two groups, it is supposed that the $CH_3{\cdot}CO_2$ group liberated at the anode combines with the salt in the solution to form the acetate of the higher oxide. These salts are readily decomposed by water; cobalt triacetate, for example, would give cobalt acetate, acetic acid, and oxygen, whilst lead tetracetate yields acetic acid and lead peroxide. From this point of view, the formation of lead peroxide in an accumulator is preceded by the formation of the salt, $Pb(SO_4)_2$, containing quadrivalent lead. T. E.

Theory of Accumulators. By WALTHER LÖB (*Zeit. Elektrochem.*, 1896, **3**, 100).—According to the views put forward by Elbs (preceding abstract) equivalent quantities of lead and lead peroxide should separate at the electrodes when a solution of lead acetate is electrolysed. The author's experiments show that this is not in general the case; by using a large anode, the greater part of the lead may be deposited as peroxide. To explain this anomaly, Elbs supposes that lead tetracetate diffuses from the anode to the cathode, and there dissolves the lead.

The author rejects this explanation, because if lead tetractate were distributed through the whole solution, lead peroxide should not separate only at the anode. [Even if lead tetracetate acted in the way supposed by Elbs, equivalent quantities of lead and lead peroxide would be found, only they would not be equivalent to the quantity of electricity passed through the cell.—ABSTRACTOR].

The author thinks that the phenomena are most readily explained by supposing that the solution contains the ion $\bar{P}b\bar{O}_2$, which need be present only in very small quantity, and which may be produced by the hydrolytic decomposition of the lead salt. T. E.

Action of Hydrochloric Acid on Metallic Sodium at Low Temperatures. By ERNST DORN and B. VÖLLMER (*Ann. Phys. Chem.*, 1897, [ii], 60, 468—477).—Pictet's observation that hydrochloric acid is without action on metallic sodium at $-80°$, led the authors to a further examination of the behaviour of hydrochloric acid at low temperatures. The acid used had a specific gravity of 1·1211 at 18°, and therefore contained 24·3 per cent. HCl. The electrical conductivity of this acid was found to decrease with falling temperature until, at $-82·2°$, the conductivity was only about $\frac{1}{35}$th of that at 18°; the conductivity curve is given by the following equation: $\nu = 10^{-8}[5065·0 + 95·753t + 0·2706t^2 - 0·002084t^3]$. The decrease in conductivity appears to be mainly due to the increase in viscocity, as the viscosity at $-80°$ is found to be about 55 times greater than that at 18°. The density of the solution was measured at $-16°$, and found to be 1·137 and again at $-78·4°$, when the value 1·174 was obtained. The E.M.F. of the combination Na | HCl | Pt is 3·018 volts. at $-80°$, the solution pressure of sodium is, therefore, still very considerable at $-80°$. This suggests that the chemical action of sodium on hydrochloric acid does not entirely cease, but is merely retarded at the above temperature. Examination of the solution showed that, as a matter of fact, sodium chloride is produced in appreciable quantity, and that action is retarded, but not completely stopped. H. C.

Specific Gravity and Electrical Conductivity of Normal Solutions of Sodium and Potassium Hydroxides, and of Hydrochloric, Sulphuric, Nitric, and Oxalic Acids. By E. H. LOOMIS (*Ann. Phys. Chem.*, 1897, [ii], 60, 547—551).—The following table contains the specific gravities and the electrical conductivities in mercury units of the solutions examined:

	Sp. gr. 18°/4°.	$K \times 10^7$ at 18°.
NaOH	1·0418	145
KOH	1·0481	170
HCl	1·0165	279
HNO_3	1·0324	278_5
$\frac{1}{2}H_2SO_4$	1·0306	183
$\frac{1}{2}C_2H_2O_4$	1·0199	55

H. C.

Electrolytic Conductivity of Solid Substances. By CARL FRITSCH (*Ann. Phys. Chem.*, 1897, [ii], 60, 300—313).—The author has determined the conductivity of a number of solid substances, taken either in the form of precipitates or compressed plates, and further

examined the effect which the addition of small quantities of a foreign solid has on the conductivity of the pure solid under examination. The effect of the addition of small quantities of a second salt to that which is under examination is in nearly all cases to largely increase the electrolytic conductivity of the latter; this would appear to be best explained by assuming the formation of a solid solution, in which the solvent, lead chloride, for example, causes ionisation of the dissolved salt, say potassium chloride. It is not impossible that the conductivity of the solid salts themselves is caused by the presence of traces of impurities, but this point would require specially investigating in each case. The conductivity increases rapidly with rising temperature, but the changes in the temperature coefficients are much smaller than those in the conductivities themselves. H. C.

The Number of Ions in some Ammonia Cobalt Compounds. By EMIL PETERSEN (*Zeit. physikal. Chem.*, 1897, **22**, 410—423).—Werner and Miolati, in their determinations of the ions in ammoniacal cobalt compounds (this vol., ii, 100), took into account only the molecular conductivity, whereas observations on the osmotic pressure are also necessary. The author has therefore determined both freezing point depression and molecular conductivity at 0° and various concentrations. From the molecular depression, by division by 18·7, the Van't Hoff coefficient, i, is obtained, and hence the number of ions, k, can be calculated from the equation $i = 1 + (k - 1)\alpha$ where α is the degree of dissociation. Dinitrotriamminocobalt chloride is thus found to form three ions, the nitrite, however, being undissociated, the latter result being in agreement with Werner's views. Dinitrotetramminocobalt nitrate forms four ions, a similar result being obtained for dichlorotetramminocobalt chloride and nitrate, dibromethylenediamminocobalt nitrate, dichlorethylenediamminocobalt chloride and nitrate, and for the chloronitrotetramminocobalt chloride; the dichlorethylenediamminocobalt bromide differing from the other praseo-salts by only forming three ions. The author does not consider, however, that these results, which indicate only the number, justify speculations on the nature of the ions. L. M. J.

Measurement of Great Electrolytic Resistances with a Constant Current. By R. MALMSTRÖM (*Zeit. physikal. Chem.*, 1897, **22**, 331—335).—The method suggested by Wilderman (Abstr., 1894, ii, 375) for the determination of electrolytic resistance is open to several practical objections, notably the difficulty of obtaining a sufficiently high constant electromotic force. The author has, therefore, examined the method suggested by Nernst (Abstr., 1894, ii, 437) and finds for resistances of 1000 ohms and upwards it is accurate and convenient, and preferable to either the ordinary Kohlrausch method or to that adopted by Wilderman. L. M. J.

Colours Produced by the Cathode Discharge in some Salts. By EUGEN GOLDSTEIN (*Ann. Phys. Chem.*, 1897, [ii], **60**, 491—499).—In a former paper (Abstr., 1895, ii, 150), the author recorded certain remarkable colour changes which salts undergo when under the influence of the cathode discharge. These changes were regarded as fairly permanent if the salt was preserved in a vacuum, but a further

series of observations have been made on this point. From these it appears that the coloured salt loses its colour again in a short time under the influence of light, but that in the dark it can be preserved for an indefinite time without undergoing change. The change under the influence of light is so marked and rapid that these coloured salts must be regarded as some of the most sensitive compounds known. The action of light is hastened and assisted by that of heat.

H. C.

Electrical Anomaly and Chemical Constitution. By PAUL DRUDE (*Ann. Phys. Chem.*, 1897, [ii], **60**, 500—509).—Certain liquids are found to possess an anomalous absorption for rapid electrical vibrations and an anomalous dispersion of their electrical indices of refraction (ratio of the wave-length of the vibration in air to that in the compound under investigation). This anomalous absorption appears to be intimately connected with chemical constitution, for the hydrocarbons, the ethers, the ketones, and aldehydes behave normally, but alcohols and acids, and generally compounds containing the hydroxyl group, possess an anomalous absorption. The differences are so marked that in many cases this property would probably be of service in settling vexed questions of constitution. An examination of ethylic acetoacetate, for example, shows that, as this compound possesses a normal behaviour, it cannot be regarded as containing the hydroxyl group. Ethylic aceto-oxalate, on the other hand, appears from the results obtained to contain hydroxyl. An exception to the above rule appears in the case of water, the behaviour of which is perfectly normal. Where an anomalous behaviour is noticed for the liquid, this appears to be maintained also by the compound in the solid state.

H. C.

Chemical Action of Electrical Oscillations. By ALEXANDER DE HEMPTINNE (*Zeit. physikal. Chem.*, 1897, **22**, 360—372).—The apparatus employed for the production of the oscillations was similar to that of Lecher (*Ann. Phys. Chem.*, 1890, [ii], **41**, 850), and allowed of the ready alteration of the wave-length. A Wimshurst machine driven at constant speed by a motor was employed in most cases, but where greater tension was required, a Tesla transformer was used. Researches with ammonia at pressures of 5 mm., 15 mm., and 50 mm. showed that the velocity of decomposition decreases with increasing pressure, and a maximum was obtained in each case some time after the commencement of the decomposition, after which it decreased, indicating a final equilibrium. The velocity is also markedly influenced by the energy of the discharge. The percentage of ammonia finally decomposed varies with the pressure, being about 50 per cent. at 49 mm. and 95 per cent. at 20 mm., but the values do not agree with the expression $p_3^2 = kp_1 p_2^3$, which should theoretically obtain in the case of a heat dissociation. The decomposition is further lowered by the addition of nitrogen or hydrogen, the latter having, as expected, the greater effect, but the quantitative results are not in accord with theoretical deductions. Under the influence of electrical oscillations, nitrogen and hydrogen combine to the extent of 3 or 4 per cent., the final quantity being apparently almost independent of the pressure. In all these cases, no action occurs unless the tube containing the gas becomes luminous; and it was

observed that one tube may screen another, so that if two tubes at slightly different pressures be placed between the plates and the discharge adjusted so that only one tube lightens, a slight increase of pressure in this tube causes it to become dark, and the second tube to lighten and be decomposed. Carbon bisulphide is also decomposed, the velocity being well represented by the equation $dx/dt = k(a - x)$. Some thick liquids, such as glycerol, exhibit an increase of vapour pressure when exposed to the action of the oscillations, a similar effect occurring with oxalic acid, whilst calcium chloride appears to be entirely unaffected. L. M. J.

The Melting Points of some Organic Compounds. By BERNHARD VON SCHNEIDER (*Zeit. physikal. Chem.*, 1897, **22**, 225—236).—The author adds a large number of melting point determinations to those previously published (Abstr., 1896, ii, 290). The values for anisoil and phenetoil were obtained as $-37.8°$ and $-33.5°$, although Haase states that they become gelatinous at $-75°$, and the author further considers several of Haase's determinations to be too low, probably owing to the use of a capillary tube. Henry's law regarding the rise and fall of the melting points of the ethereal salts of the oxalic series was found to hold for both methylic and ethylic salts, a similar relationship obtaining in the case of the chloro- and bromo-derivatives of acetic acid and the corresponding amides, as well as for the chloro-derivatives of benzene and toluene. Dewar (Roy. Inst., Jan., 1894), classes turpentine, ethylic nitrate, and quinoline among compounds which form glassy masses, but the author found they solidified as crystalline masses at the temperatures $-65°$, $-112°$, and $-19.5°$ respectively. He, however, finds, like Dewar, that some compounds solidify to glassy masses. The author further verifies Petersen's conclusion, that chloro-compounds have a lower melting point than bromo-compounds, and these lower than the iodo-compounds; also that the chlorides melt at lower temperatures than the corresponding cyanides. The determinations are as follows:—diethylic oxalate, $-41°$; ethylenic dichloride, $-36°$; ethylenic chlorobromide, $-16.6°$; ethylenic chloriodide, $-15.6°$; chlorobenzene, $-45°$, bromobenzene, $-30.5°$, iodobenzene, $-28.5°$; benzonitrile, $-12.9°$; diethylaniline, $-38.8°$; paraphenetidine, $+2.4°$; orthonitrotoluene, $-14.8°$; anisoil, $-37.8°$, ethylthiocarbimide, $-5.9°$; chlorpicrin, $-69.2°$; ethylic salicylate, $+1.3°$; ethylic chloride, $-142.5°$; ethylic bromide, $-125.5°$; ethylic iodide, $-118°$; ethylidenic chloride, $-101.5°$; ethylic nitrate, $-112°$; propionitrile, $-103.5°$; diethylic malonate, $-49.8°$; diethylic succinate, $-20.8°$; benzylic cyanide, $-24.6°$; methylic salicylate, $-8.3°$; phenetoil, $-33.5°$; butyric acid, $-7.9°$; propionic acid, $-22°$; benzylic chloride, $-43.2°$, benzylidenic chloride, $-16.1°$; benzotrichloride, $-21.2°$; phenylthiocarbimide, $-21°$; orthanisidine, $+5.2°$; acetonitrile, $-44.4°$. A few compounds changed to glassy masses at below $-80°$.
L. M. J.

Determination of Freezing Points. By J. A. HARKER (*Proc. Roy. Soc.*, 1896, **60**, 154—156).—The methods at present in use for the determination of the freezing point are unsatisfactory, and cannot be depended on to more than 0·001° to 0·002°. The author describes a method, consisting essentially of cooling the liquid to slightly below

its freezing point, dropping in a crystal of the solid, and observing the temperature with the aid of a modified platinum thermometer. By this means more consistent results, agreeing to within one or two ten-thousandths of a degree, may be obtained. A. W. C.

Former Determinations of Freezing Points. By LOUIS C. DE COPPET (*Zeit. physikal. Chem.*, 1897, **22**, 239—240).—The author, considering his determinations of freezing points (1871) of saturated solutions to be comparatively unknown, republishes the numbers, which are given below, together with the weight of anhydrous salt per 100 parts of water:—KCl, −11·1°, 24·6; NaCl, −21·8°, 29·6; NH_4Cl, −15·8°, 22·9; $SrCl_2$, −18·7°,—; $BaCl_2 + 2H_2O$, −7·8°, 25·1; $ZnSO_4 + 7H_2O$, −6·5°, 37·3; $CuSO_4 + 5H_2O$, −1·6°, 13·5; $(NH_4)_2SO_4$ −19·05°, 62·2; K_2CrO_4, −11·3°, 57·7; $Na_2SO_4 + 10H_2O$, −1·2°, 4·0; $Na_2SO_4 + 7H_2O$, −3·5°, 14·5; $Na_2CO_3 + 10H_2O$, −2·1°, 5·3; KNO_3, −2·85°, 10·7; $NaNO_3$, −18·5°, 58·5; NH_4NO_3, −17·3°, 70·0; $Ba(NO_3)_2$, −0·7°, 4·5; $Sr(NO_3)_2$, −5·7°, 32·4; $Pb(NO_3)_2$, −2·7°, 35·2. L. M. J.

Freezing Points of Dilute Aqueous Solutions. III. By E. H. LOOMIS (*Ann. Phys. Chem.*, 1897, [ii], **60**, 523—546. Compare Abstr., 1896, ii, 352).—The author has continued his researches on the freezing points of dilute aqueous solutions, and in the results here brought forward claims an accuracy to within 0·0005°. Solutions of the chlorides of lithium, calcium, and strontium give molecular depressions, which at first decrease with rising dilution, and after attaining a minimum value again increase. Stannic chloride in the most dilute solution examined gives a molecular reduction of 126·1. As a compound containing five ions could not give, even on complete electrolytic dissociation, a greater reduction than 94·5, the author concludes that stannic chloride decomposes in aqueous solution, and perhaps forms $SnCl_2$ and 2HCl. The behaviour of phosphoric acid, which gives a molecular reduction of 28·2 in the most dilute solution examined, is taken as indicating that this compound dissociates into the ions H and H_2PO_4. In keeping with this, it appears that KH_2PO_4 also dissociates into the two ions K and H_2PO_4, but the behaviour of Na_2HPO_4 is best explained by its dissociation into the *three* ions, Na, Na, and HPO_4; and Na_3PO_4 from the cryoscopic results must be regarded as dissociated into *four* ions. Sodium silicate, Na_2SiO_3, like stannic chloride, gives a much greater molecular depression than would accord with the dissociation hypothesis. The organic acids, acetic, oxalic, succinic, tartaric, and citric, all behave as electrolytes, and not as non-electrolytes. Acetic acid, in its more concentrated solutions, acts, however, as a non-electrolyte, the molecular depression increasing regularly with the concentration. A comparison of the results obtained with the values deduced from the Van't Hoff and Arrhenius theories shows that there is a complete accordance for the chlorides of lithium and calcium. A satisfactory agreement is obtained with acetic, tartaric, and citric acids, and the agreement is also fair in the case of strontium chloride. On the other hand, the values for HNO_3, KOH, and NaOH do not agree with those demanded by the dissociation hypothesis, differences of from 8 to 11 per cent. being obtained in the

most dilute solutions. The differences are, curiously enough, less for the more concentrated solutions. H. C.

Aniline in Cryoscopy. By G. Ampola and C. Rimatori (*Gazzetta*, 1897, **27**, i, 35—51).—The authors have made series of determinations of the depressions of the freezing point of aniline by bromobenzene, bromotoluene, nitrobenzene, chloroform, bromoform, ethylenic bromide, benzene, toluene, paraxylene, thiophen, benzaldehyde, ethylic oxalate, pyridine, piperidine, dimethylaniline, quinoline, ortho- and para-toluidine, coniine, valeric acid, isobutyric acid, phenol, cresol, carvacrol, thymol, methylic alcohol, ethylic alcohol, caprylic alcohol, benzylic alcohol, isobutyric alcohol, and the diethylic ether of glycerol. The molecular depression calculated as the mean from those cases in which the behaviour is most regular is 58·67, whilst the value calculated by Raoult's rule is 57·66.

Aniline differs considerably from dimethylaniline as a solvent in cryoscopy (compare following abstract) in that its behaviour is more like that of acid solvents such as acetic acid; compounds containing hydroxyl give molecular depressions in aniline which do not appreciably differ from those given by compounds containing no hydroxyl. This analogy of behaviour also extends to fairly concentrated solutions, excepting in the case of aniline solutions of methylic, ethylic, and isobutyric alcohols, when greater deviations than usual from the law are observed. Ethylenic bromide and benzaldehyde behave abnormally, owing probably to their combining with the solvent. W. J. P.

Dimethylaniline in Cryoscopy. By G. Ampola and C. Rimatori (*Gazzetta*, 1897, **27**, i, 51—68).—The authors have determined the depressions of the freezing point of dimethylaniline caused by benzene, toluene, paraxylene, thiophen, bromotoluene, chloroform, bromoform, benzaldehyde, nitrobenzene, bromobenzene, bromotoluene, veratrol, ethylic oxalate, ethylenic bromide, methylic alcohol, isobutylic alcohol, trimethylcarbinol, benzylic alcohol, caprylic alcohol, the diethylic ether of glycerol, pyridine, piperidine, aniline, quinoline, orthotoluidine, formic acid, isobutyric acid, valeric acid, phenol, paracresol, thymol, and carvacrol. The mean molecular depression of the freezing point of dimethylaniline calculated from the most suitable of the above determinations is 58, whilst that calculated by Raoult's rule is 75·02.

Most substances behave fairly regularly in dimethylaniline solution, and as a solvent this base resembles the hydrocarbons and their halogen derivatives. The molecular depression of the freezing point caused by the alcohols is nearly normal in dilute solutions and diminishes rapidly as the concentration increases, being only 7 in a 25 per cent. solution of methylic alcohol in dimethylaniline. Phenol and paracresol give low molecular depressions, which diminish as the concentration increases although not so rapidly as in the case of the alcohols; thymol, carvacrol, and the alkaloids show fairly normal behaviour. Formic acid behaves much like methylic alcohol, and the acids generally behave more regularly as their molecular weights rise. The hydrocarbons, ethers, and aldehydes give molecular depressions greater than the normal in dilute solution, and as the concentration increases the molecular depressions assume less than the normal value. W. J. P.

Calculation of Heats of Dissociation and Combination Based on a Theory of Valency and Affinity. By JOACHIM SPERBER (*Zeit. anorg. Chem.*, 1897, **14**, 164—171).—Upon certain speculations with reference to valency and affinity, the author bases calculations of the heats of dissociation and combination of some of the elements. The heat of dissociation of chlorine is given as 44 Cal., and the heat of combination of hydrogen with chlorine as 66 Cal. The heat of dissociation of an equivalent of oxygen is calculated as 83·9 Cal., and the heat of combination of an equivalent of oxygen with hydrogen as 112·7 Cal.

H. C.

Change of Free Energy in the Formation of Insoluble Mercury Compounds. By STEFAN BUGARSZKY (*Zeit. anorg. Chem.*, 1897, **14**, 145—163).—By measuring the E.M.F. of certain cells, in which mercurous salts react with soluble electrolytes producing insoluble mercurous compounds, the author determines the change of free energy in the reactions. This is compared with the total energy change, the results obtained, given in heat units, being as follows:

Reaction.	Total energy.	Free energy.
$HgCl + KBr$	4010 cal.	2971 cal.
$HgC_2H_3O_2 + KBr$	12000 "	6906 "
$HgCl + KI$ (yellow iodide)	9310 "	7134 "
$HgCl + KI$ (greenish-yellow iodide)	9160 "	7127 "
$HgC_2H_3O_2 + KI$	17275 "	9883 "
$2HgCl + 2KOH$	– 3280 "	7566 "
$2HgC_2H_3O_2 + 2KOH$	13270 "	12138 "
$Hg_2SO_4 + 2KCl$	23330 "	13940 "
$2HgCl + 2KSH$	23550 "	41348 "
$HgNO_3 + KCl$	12160 "	6930 "

The soluble electrolytes were employed in centinormal solution.

H. C.

Absolute Determination of the Expansion of Water. By MAX THIESEN, KARL SCHEEL, and H. DIESSELHORST (*Ann. Phys. Chem.*, 1897, [ii], **60**, 340—349).—The principle of the method adopted by Regnault for the determination of the expansion of mercury, that of measuring the heights of two communicating and counterbalancing columns of the liquid maintained at different temperatures, was adopted for the determination of the expansion of water. The results obtained for the densities and volumes at different temperatures, referred to those at the point of maximum density, were as follows:

Temperature.	Density.	Volume.
0°	0·9998679	1·0001321
3·98	1·0000000	1·0000000
10	0·9997272	1·0002728
15	0·9991263	1·0008745
20	0·9982298	1·0017733
25	0·9970714	1·0029372
30	0·9956732	1·0033456
35	0·9940576	1·0059779
40	0·9922417	1·0078190

The temperatures are those of the hydrogen thermometer. H. C.

Internal Friction of Salt Solutions and Mixtures. By ARISTIDES KANITZ (*Zeit. physikal. Chem.*, 1897, 22, 336—357).—The internal friction was determined in the case of a large number of salt solutions, Ostwald's form of apparatus being employed. According to Arrhenius, the effect of dilution is given by the expression $H = A^x B^y$, where H is the friction of the mixture, A and B that of the components, and x and y their respective volumes. This equation is first tested for a number of single salts, namely, solutions of ammonia, ammonium chloride, ammonium nitrate, ammonium sulphate, potassium hydroxide, potassium carbonate, potassium dichromate, sodium hydroxide, sodium carbonate, ferric chloride, and dichloracetic acid, the concentration varying from 2N to N/8. The observed and calculated values agree well in most cases, but the values are throughout little removed from unity. The difference between the friction coefficients of the hydroxide and chloride is much less in the case of the ammonium than of the potassium salts, a result attributed to the slight dissociation of the ammonium hydroxide. The difference, however, in the case of the quaternary amines is approximately equal to that of the potassium compounds. In the amines, the friction increases with the addition of methyl or ethyl groups, except in the case of the change from the trimethyl- to tetramethyl-ammonium chloride. A large number of salt solutions were also examined; Arrhenius' formula giving on the whole results in accordance with the observations. In some cases, differences may be ascribed to dissociation changes consequent on the mixtures of the solutions; in others, to the formation of double salts, as in many solutions containing mercuric chloride. The friction in the case of ferric chloride is very great, and is probably due to hydrolytic decomposition and the formation of colloidal solutions, hence by the additions the friction is considerably less than that calculated. Molecular complexes are also probably formed in the case of mixtures of potassium or sodium and lead nitrate, or potassium or sodium and strontium nitrates, results also in accordance with previous work of Le Blanc and Noyes (Abstr., 1891, 388). L. M. J.

The Formation and Changes of Solids. By WILHELM OSTWALD (*Zeit. physikal. Chem.*, 1897, 22, 289—330).—The author first considers the solidification of overcooled melted solids and the crystallisation of supersaturated solutions, and endeavours to determine the least amount of solid which can bring about the change. Salol (melting point 39·5°) was found very convenient for the purpose, as it may be kept overcooled for weeks, although a hair, or filament of glass, that has been drawn lightly across a crystal can effect the solidification of the liquid. The hair or glass may, however, be "sterilised" by drawing a few times between the fingers, or more certainly by heating to 40°. By well mixing the salol with nine times its weight of an inactive compound, such as quartz powder, and repeating this process, the solid may be "diluted" to any desired extent, and it was found that, if freshly prepared, this dilution has to be done six times before the solid loses its specific power; but on standing for two days the D.4 was also found incapable of effecting the solidification, that is, had lost the properties of solid salol. This may be due to the salol no longer being present in the

solid state, but in the gaseous form condensed upon the surface of the diluting solid, and analogous results were obtained in other cases. The author gives to the above form of instability, where the change to solid can only be caused by the presence of the solid itself, the name of "metastabile," the term labile being applied to those cases where other causes may effect the solidification, as in the case of most liquids cooled much below the melting point. The general law is stated that, during a transition from a particular state to one of greater stability, the change is not necessarily to the most stable but to the nearest. This law is illustrated by a large number of examples, such as the solidification of melted sulphur to the monoclinic and not the rhombic form, the changes of mercuric iodide, the formation of liquid drops of benzoic and other acids when precipitated by mineral acids, the production of potassium chloride and hypochlorite by the action of chlorine on potassium hydroxide, &c. The crystallisation of a supersaturated solution of sodium chlorate is more fully examined, and it is found that moisture or an unsaturated solution lowered the activity of the diluted crystals; but this was not the case with a saturated or supersaturated solution. A method of observation analogous to the 'culture' method of bacteriology is described, by which the limiting quantity of salt capable of effecting the solidification was obtained as $0{\cdot}6 \times 10^{-10}$. Similar work with alums, sodium potassium tartrate, borax, and barium chloride is recorded, the necessary dilution of the solid and the time elapsing before crystallisation being found to vary greatly. The capability of effecting crystallisation is, the author considers, a most convenient and certain test for isomorphism; thus, overcooled melted metachloronitrobenzene solidifies on the addition of metabromonitrobenzene, but not on the addition of either the parachloro- or parabromo-compound. L. M. J.

Inflammability of Explosive Mixtures of Gases. By FRIEDRICH EMICH (*Monatsh.*, 1897, 18, 6—26).—When the mixture of hydrogen and oxygen obtained by the electrolysis of water is exploded, a small residue always escapes combustion; this probably existed as a layer coating the walls of the vessel, by which it was so far cooled that the explosion was no longer propagated in it. In order to obtain an approximate estimation of the thickness of this layer, electrodes were constructed consisting of pointed aluminium (or platinum) wires of 1 mm. diameter enclosed in glass capillary tubes, the ends of which were ground flat so that the terminal points of the wires lay in the centre of the plane glass surfaces thus produced. These electrodes were placed opposite each other, and so as to penetrate vertically the walls of a horizontal thick glass tube; the lower electrode was cemented in the wall, the upper could be moved up and down through a stuffing-box by means of a micrometer screw. The horizontal tube having been filled with the gaseous mixture, the upper electrode was made to touch the lower one; it was then screwed back a little at a time, and at each resting-place a spark was passed. At first, the very short sparks obtained were unable to bring about an explosion of the gas; as soon as an explosion occurred, the distance apart of the electrodes was noted, and this was taken as the length of the shortest spark that

would produce an explosion of the mixture in question. With electrodes of 5·5 mm. diameter, this length was 0·22 mm. in a mixture of 2 vols. of hydrogen with 1 vol. of oxygen under normal conditions; and since the distance apart of the two flat surfaces of the electrodes was small in comparison with the dimensions of the surfaces, this distance may be taken as the thickness of the layer in which the explosion can only just propagate itself. This distance is independent of the metal of the electrode; with electrodes of smaller diameter (2·0 mm.), it is found to be slightly less, but a diameter of 2·7 mm. suffices to give the same result as one of 5·5 mm.

The more easily inflammable a gaseous mixture is, the shorter will be the spark that is just able to explode it. Defining inflammability in this way as inversely proportional to the minimum length of spark necessary for explosion, it is found that, with mixtures of hydrogen and oxygen in the proportions of 2 : 1 and 1 : 1 by volume, and under pressures varying from 730 mm. to 156 mm., the inflammability is nearly proportional to the pressure, but increases rather more rapidly. The effect of temperature is small; an increase from the ordinary temperature to 380° only increases the inflammability by $\frac{1}{7}$th.

It is found that dilution of the electrolytic mixture of hydrogen and oxygen (2 : 1 by volume) with oxygen actually increases the inflammability, the maximum inflammability being attained when the gases are present in equal proportions by volume. Dilution with hydrogen, nitrogen, or carbonic anhydride at first occasions a slight increase of inflammability, and finally a decrease, comparison being made with pure electrolytic gas under a pressure equal to its partial pressure in the diluted sample. C. F. B.

Affinity Constants and Constitution of Organic Acids. By Bohdan Szyszkowski (*Zeit. physikal. Chem.*, 1897, **22**, 173—188).—The first series of acids investigated were chiefly derivatives of hydracrylic acid, the molecular conductivity and affinity constants being determined at 25°. In compounds containing secondary hydroxyl, the substitution of an alkyl group for hydrogen causes in general a decrease of the affinity constant, whilst the introduction of phenyl gives rise to a very marked increase. In acids containing tertiary hydroxyl, displacement of the hydrogen by hydrocarbon radicles always causes a slight increase, so that the effect of substitution by one and the same substituent is not dependent on its electrochemical character only. The constants of the secondary compounds are also throughout considerably less than those of the corresponding tertiary compounds. The affinity constants of unsaturated acids are considerably greater than those of the corresponding saturated acids, whilst the passage to the acetylenic compound is marked by a still further increase. As the constant also increases with approach of the electronegative groups, the author considers it probable that doubly-linked carbon atoms are nearer together than singly-linked atoms, whilst the triple linking indicates still greater proximity, the great instability of the latter compounds being due to this fact and the electrical repulsion of the atoms. The methyl group is also considered to be more electronegative

than hydrogen, and iso-radicles are more electronegative than those with normal structure. L. M. J.

Velocity of the Reaction between Ferrous Chloride, Potassium Chlorate, and Hydrogen Chloride. By ARTHUR A. NOYES and R. S. WASON (*Zeit. physikal. Chem.*, 1897, **22**, 210—221).—The reaction between ferrous sulphate and potassium chlorate in the presence of excess of sulphuric acid was found by Hood (Abstr., 1886, 301) to be of the second order, the velocity being proportional to the product of the concentrations of the two salts, the acid exerting an accelerative influence, the velocity increasing more rapidly than the acid concentration. The authors have studied the simpler case of the chlorides, and determined the velocity of reaction for several different sets of experiments, the velocity being calculated for both second order and third order reactions. Although with excess of acid the equation for a reaction of the second order apparently gives a satisfactory constant, yet the reaction is seen to be of the third order, this constant only varying irregularly from 157 to 184 through the whole set of experiments, whereas the second order constant increased regularly from 343 to 2130, whilst the acid concentration increased from n/10 to n/2. The actual course of the reaction, however, is not evident, as apparently more than three molecules of the compounds interact. The effect of temperature was investigated by means of a series of researches at 0°, 10°, 20°, 30°, 40°, and 50°, and the equation $\log K_1/K_2 = A(T_1 - T_2)/T_1T_2$ was found to give a constant value for A; this result accords with Van't Hoff's expression $d \log K/dt = A/T^2 + B$ when $B = 0$, which obtains in many other reactions (Abstr., 1889, 1044, 1103).

L. M. J.

Velocity of Formation and Decomposition of Ethereal Salts. By OSC. KNOBLAUCH (*Zeit. physikal. Chem.*, 1897, **22**, 268—276).—The reaction $C_2H_5 \cdot OH + CH_3 \cdot COOH \rightleftarrows CH_3 \cdot COOC_2H_5 + H_2O$ was investigated in order to determine whether the velocity of decomposition of the ethereal salt obtained by a direct determination was actually equal to that deduced by calculation from the interaction of the alcohol and acid. By the 'direct' action, the ratio of the direct and inverse velocities was found to be 2·81, and from the 'inverse' action the ratio 2·67 was obtained, the mean value 2·74 being afterwards used in the calculations. By this means, the value $1{\cdot}01 \times 10^{-4}$ was obtained for the inverse (decomposition) velocity by calculation from the 'direct' reaction, and the value $0{\cdot}99 \times 10^{-4}$ was obtained from the measurement of the velocity of decomposition, the agreement being well within the experimental limits. L. M. J.

Chemical Proportions. By F. WALD (*Zeit. physikal. Chem.*, 1897, **22**, 253—267).—The author gives an account and explanation of the generally accepted laws of the atomic theory, and endeavours to prove that in compounds derived by the interaction of others the law of multiple proportions must hold, or as he finally states it: "If in a series of chemical compounds containing one common constituent we take such quantities that this constituent is present in equal quantity in all,

then the quantities of any other constituent which occur in different members of the series have a rational greatest common measure."

L. M. J.

Inorganic Chemistry.

A Convenient Method for Purifying Water. By HARRY C. JONES and E. MACKAY (*Zeit. physikal. Chem.*, 1897, **22**, 237—238).—To obtain water suitable for physico-chemical measurements, the authors add some potassium permanganate and sulphuric acid to ordinary distilled water, and distil from a large flask. The vapour is passed into a retort sloping upwards, and containing distilled water, with potassium permanganate and sodium hydroxide; the end of the neck is packed with glass wool, and fitted with a receiver passing to a block tin condenser. No corks are employed, all packing being made with asbestos, and the glass wool is washed with hydrochloric acid, and heated in a stream of hydrogen. The first portion of the distillate is neglected, as it contains small quantities of ammonia, and large quantities can then be readily obtained with a conductivity of about $1\cdot5—2\cdot0 \times 10^{-6}$. L. M. J.

Fluoroxyiodates. By RUDOLPH F. WEINLAND and O. LAUENSTEIN (*Ber.*, 1897, **30**, 866—869).—By the action of a 40 per cent. solution of hydrofluoric acid on iodates of the alkali metals and of ammonium, an oxygen atom is replaced by fluorine, the resulting difluoroxyiodates being well-defined crystalline substances. *Potassium difluoroxyiodate*, KIO_2Fl_2, forms large, colourless prisms, which in the dry condition are tolerably stable, but when exposed to moist air readily split up into the iodate and hydrofluoric acid. When heated, the difluoroxyiodate first melts and then decomposes, iodine and oxygen being evolved. Calcium chloride gives a precipitate of calcium fluoride, with a dilute aqueous solution of the salt.

Ammonium difluoroxyiodate, $NH_4IO_2Fl_2$, has the same crystalline form as the potassium salt, and behaves similarly to it, except when heated. *Sodium difluoroxyiodate* forms thin, hexagonal plates.

Contrary to the observation of Ditte, the authors find that iodic acid is without action on hydrofluoric acid, even when heated, the iodic acid being always recovered unchanged. Other fluoroxyiodates are being investigated. J. F. T.

Conditions of the Direct Combination of Hydrogen and Sulphur. By H. PÉLABON (*Compt. rend.*, 1897, **124**, 686—688).—At 440°, the direct combination of hydrogen and sulphur is limited by the reverse reaction, and between 215° and 350° it is also limited, but not by the reverse reaction, since hydrogen sulphide is not decomposed by heat between these limits of temperature. Experiments have therefore been made with a view to ascertain the conditions of direct combination at temperatures below 440°. When hydrogen and sulphur are heated in sealed tubes which are opened after being allowed to cool,

the final composition of the gaseous mixture depends on the mass of sulphur employed, and the proportion of hydrogen sulphide is higher the higher the proportion of sulphur. The composition of the gaseous mixture in the cooled tube corresponds the more nearly with that of the gaseous mixture at the temperature of the experiment, the smaller the mass of the sulphur. When the proportion of the sulphur is low, but yet in excess, combination takes place more quickly the higher the temperature, and the maximum quantity of hydrogen sulphide that can be formed increases very regularly with the temperature. Experiments with larger masses of sulphur show that the quantity of hydrogen sulphide dissolved by the fused sulphur increases with the temperature. When the hydrogen is mixed with nitrogen, the maximum quantity of hydrogen sulphide formed is less than with pure hydrogen for the same time of heating, but, other conditions being the same, the difference is smaller the higher the temperature (compare this vol., ii, 207).

C. H. B.

Sulphuryl Chloride. By BRONISLAW PAWLEWSKI (*Ber.*, 1897, **30**, 765—767).—Owing to the literature of the subject being somewhat confused, the author considered it necessary to reinvestigate the properties of this compound. It boils (pressure = 760 mm.) at 69·1—69·2°, and has a sp. gr. = 1·66738, at 4°/20°; its refractive index $R_M = 35·92$, and its critical temperature after the first heating lies between 217—252°, depending on the quantity of liquid in the tube. The dissociation of the compound begins at 160°, and at 240—250° the vapour density is no longer normal.

J. F. T.

The Freezing Point of Dilute Sulphuric Acid. By WILHELM HILLMAYR (*Monatsh.*, 1897, **18**, 27—33).—The following results were obtained:

Percentage of sulphuric acid	1·95	3·00	4·01	5·13	6·02	8·02.
Freezing point ...	−0·78°	−1·16°	−1·65°	−2·05°	−2·55°	−3·61°.

These results agree well with those of Pfaundler and Schnegg (*Sitzungsber. Kaiserl. Akad. Wiss.*, 1875, **71**), and differ from those of Pictet (Abstr., 1895, ii, 106), who found values for the freezing point above 0°.

C. F. B.

Sodium Thioselenide. By CARL MESSINGER (*Ber.*, 1897, **30**, 805—806).—When selenium is boiled with aqueous sodium hydrosulphide in a current of hydrogen, it yields a solution from which alcohol precipitates *sodium thioselenide*, $Na_2SSe_2 + 5H_2O$, as a mass of dark red scales; the salt is hygroscopic and rapidly decomposes in the air, sodium sulphide and selenium being formed.

A. H.

Nitrogen Sulphide. By AMERICO ANDREOCCI (*Zeit. anorg. Chem.*, 1897, **14**, 246—250).—The author has commenced an examination of the chlorides of nitrogen sulphide with the object of elucidating the constitution of nitrogen sulphide. The nitrogen sulphide is prepared by the method described by Fordos Gélis (*Annalen*, 1851, **80**, 260), and melts at 178—179°. The determinations of the molecular weight by the boiling point method, using as solvents benzene and carbon

tetrachloride, agree with the formula N_4S_4, and confirm the determinations of Clever and Muthmann.

The yellow nitrogen sulphide chloride, $N_4S_4Cl_4$, is obtained by treating nitrogen sulphide suspended in carbon tetrachloride with chlorine. The chloride is stable when preserved under carbon tetrachloride, and crystallises without decomposition from hot, dry benzene. Determinations of the molecular weight by the cryoscopic method, using benzene as solvent, agree with the formula $N_4S_4Cl_4$. When the benzene solution is treated with water, it decomposes, and yields sulphurous anhydride and nitrogen chloride. When, however, it is treated directly with such a quantity of water that no appreciable rise in temperature takes place, it also yields an insoluble powder which contains nitrogen sulphide. When warmed, it yields the red chloride and other compounds; by the action of cold ammonia, it is reconverted into nitrogen sulphide, and is decomposed by absolute methylic and ethylic alcohols and phenol. When treated with dry hydrogen chloride in benzene solution, it yields a bright yellow compound which is only slowly decomposed by cold water, but immediately by lukewarm water.

E. C. R.

Seleno-arsenates. By CARL MESSINGER (*Ber.*, 1897, **30**, 797—805).—The author has prepared a number of salts intermediate between sodium arsenate, thioarsenate and selenarsenate by the action of the sodium compounds of sulphur, selenium, and oxygen on the selenosulphides of arsenic and in other similar ways. $Na_3AsO_2SSe + 10H_2O$ is prepared by the action of aqueous soda on arsenic triselenobisulphide, and crystallises in white, matted needles which decompose in the air. Acids cause the precipitation of sulphur and selenium from its solution. When arsenic diselenotrisulphide is dissolved in aqueous soda, the *salt* $Na_6As_2SeS_3O_4 + 20H_2O$ is produced in colourless, radiating needles which are tolerably stable in dry air. The mother liquor from this salt contains a *salt*, $Na_6As_2S_3Se_2O_3 + 20H_2O$, which crystallises in colourless needles. The *salt* $Na_6As_2S_7Se + 16H_2O$ is formed when arsenic diselenotrisulphide is treated with aqueous sodium hydrosulphide; the yellow prisms are stable in dry air, and acids precipitate arsenic trisulphide and sulphur from its solution. The *salt* $Na_3AsS_3Se + 8H_2O$ is produced when arsenic triselenodisulphide is treated with aqueous sodium hydrosulphide, and crystallises in well developed prisms; acids precipitate arsenic diselenotrisulphide from its solution. The *salt* $Na_3AsS_2Se_2 + 9H_2O$ is formed when arsenic triselenide (1 mol.) is fused with selenium (1 atom) and sulphur (1 atom) and the whole dissolved in sodium hydrosulphide; it crystallises in reddish-yellow prisms, and is decomposed in solution by dilute acids with evolution of hydrogen selenide and sulphide, whilst sulphur, selenium, and the triselenide and trisulphide of arsenic are deposited.

The *salt* $Na_3AsSSe_3 + 9H_2O$ is formed together with sodium monoselenothioarsenate when arsenic triselenide is dissolved in a mixture of sodium thioselenide and sulphide; it crystallises in red, hygroscopic prisms, and is decomposed by aqueous acids with evolution of hydrogen selenide and sulphide and precipitation of arsenic trisulphide and selenium. The *salt* $Na_9As_3S_2Se_2O_8 + 36H_2O$, obtained by dissolving arsenious oxide, sulphur, and selenium in aqueous soda, crystallises in

large, white prisms and is decomposed by aqueous acids with precipitation of sulphur and selenium, whilst a sulphoxy-salt remains in solution. The mother liquor from this salt contains the salt $Na_6As_2S_2SeO_5 + 24H_2O$, which closely resembles the foregoing. The *salt* $Na_6As_2S_5Se_3 + 16H_2O$ is obtained in brownish-yellow prisms by boiling sodium diselenothioarsenate, $Na_3AsS_2Se_2$, with sodium hydrosulphide, 2 molecules of the latter being necessary to replace a single atom of selenium by sulphur. It appears from a comparison of the solubilities of these salts that an arsenate is more soluble the greater the molecular weight of the acid residue contained in it. A. H.

Conversion of Diamond into Graphite in a Crookes' Tube. By HENRI MOISSAN (*Compt. rend.*, 1897, **124**, 653—655).—Diamonds which had been subjected to molecular bombardment in a Crookes' tube were completely blackened on the surface, and after prolonged treatment with nitric acid and potassium chlorate yielded graphitic oxide, which, when heated, changed into pyrographitic acid. The graphite was very slowly oxidised, and in this respect behaved like graphite formed at a high temperature. After four treatments with the oxidising mixture, the diamonds were still covered with a maroon-brown film of finely-divided carbon.

Since diamond is not converted into graphite in the oxyhydrogen blow-pipe, it is clear that the molecular bombardment must produce a temperature which exceeds 2000°. The behaviour of the graphite, in fact, indicates that it has been formed at a temperature similar to that of the electric arc, or about 3600°. C. H. B.

Helium and Argon. III. Experiments which show the Inactivity of these Elements. By WILLIAM RAMSAY and J. NORMAN COLLIE (*Proc. Roy. Soc.*, 1896, **60**, 53—56).—The paper contains a record of a number of experiments made to test the possibility of forming compounds of helium and argon.

On maintaining an electric arc, the electrodes of which were thin pencils of gas carbon, for several hours in an atmosphere of argon, a slow expansion took place, and on sparking the resulting gas with oxygen, carbonic anhydride was produced. It was at first thought that possibly a compound of argon had been formed, but on further examination it was shown that, although apparently all gas had been removed from the carbon electrodes before admitting argon, some carbonic anhydride still remained occluded and that prolonged heating had expelled this gas and converted it into the monoxide.

By the action of producer gas on a mixture of barium carbonate and carbon at the temperature of the electric arc, a substance rich in barium cyanide is obtained, from which all the nitrogen was recovered by Dumas' process. The whole of the nitrogen disappeared in presence of oxygen and soda, leaving no residue, thus showing that no argon had entered into combination.

A mixture of argon with the vapour of carbon tetrachloride was exposed to the silent electric discharge from a powerful induction coil. Here again, although a considerable amount of other chlorides of carbon was produced, argon did not enter into the reaction, but was recovered without loss of volume.

In experimenting with helium, the gas was circulated over the reagent at a bright red heat, and observations made of any alteration in volume or any marked change in the reagent employed. In no case was there any reason to suspect that helium had entered into combination.

The following is a list of substances tried:—sodium, silicon, beryllium, zinc, cadmium, boron, yttrium, thallium, titanium, thorium, tin, lead, phosphorus, arsenic, antimony, bismuth, sulphur, selenium, uranium, chlorine, cobalt, platinum, mixtures of soda-lime and potassium nitrate and soda-lime and sulphur, and benzene.

It is pointed out that any compound of helium capable of existence will probably be endothermic, and the two methods of producing such a compound, namely, exposure to a high temperature and the influence of the silent electric discharge, have been tried in vain. It is therefore to be concluded that helium and argon are incapable of forming compounds. A. W. C.

Amount of Argon and Helium contained in the Gas from the Bath Springs. By LORD RAYLEIGH (*Proc. Roy. Soc.*, 1896, **60**, 56—57).—The refractivity found for the residue from the gas of the Bath springs after removal of all gases known until recently, was found to be 0·896 referred to air. The proportional amount of helium is, therefore, 8 per cent., or 1·2 parts per thousand of the original volume. A. W. C.

Drying and Deliquescence of Certain Salts. By F. W. SMITHER (*Amer. Chem. J.*, 1897, **19**, 227. Compare Hake, *Proc.*, 1896, **12**, 33).—Tabulated records of the relative power possessed by certain inorganic salts of absorbing and retaining moisture are given. From these it would appear that lithium chloride, which is extremely hygroscopic at ordinary temperatures, is soon rendered anhydrous when heated in a steam bath at 97—98°. Calcium chloride, under similar conditions, retains less than $1H_2O$ after from 30—40 hours' heating, and afterwards loses and regains a small fraction of this amount repeatedly. Calcium nitrate behaves in much the same way. Both the chloride and nitrate of magnesium retain $1H_2O$ obstinately, and then lose water and acid gradually, some magnesium hydroxide being formed.

When the same salts are exposed to an atmosphere nearly saturated with moisture, they continue to absorb water most conspicuously, lithium chloride taking up more than 15 times its weight. During the exposure, a period is noticed when this salt ceases to absorb moisture, and the others lose in weight, but afterwards an increase in weight is noticed in all cases.

The author concludes that these salts do not form any hydrates when in the liquid state at ordinary temperature. A. W. C.

Micrographic Study of some Italian Cements. By LORENZO BUCCA and GIUSEPPE ODDO (*Gazzetta*, 1896, **26**, ii, 549—554).—The authors have examined three Italian cements, and criticise Le Chatelier's conclusions. (Compare Oddo and Manzella, Abstr., 1896, ii, 246.) W. J. P.

Hydrates of Cadmium Sulphate. By FRANZ MYLIUS and ROBERT FUNK (*Ber.*, 1897, **30**, 824—833).—The authors confirm Etard's

work (Abstr., 1888, 645) on the solubility of ordinary crystallised cadmium sulphate, $3CdSO_4 + 8H_2O$. The solubility reaches its maximum at 74°, when the percentage of substance dissolved is 46·7; from 74° to 100°, the solubility rapidly diminishes. When a saturated solution of cadmium sulphate is slowly evaporated at 70°, large crystals of the ordinary hydrate, $3CdSO_4 + 8H_2O$, are obtained, but if evaporated at 80°, a microcrystalline powder is deposited. The same powder is obtained at 100°; it consists of the hydrate $CdSO_4 + H_2O$, and does not lose its water of crystallisation at 100°. The sudden drop in the solubility of the ordinary hydrate at 74° is no doubt due to its conversion into the hydrate $CdSO_4 + H_2O$, which, at the ordinary temperature, slowly combines with water to form the ordinary hydrate.

A new hydrate, $CdSO_4 + 7H_2O$, is obtained when a solution of cadmium sulphate, saturated at 74°, is suddenly cooled to below −17°; on raising the temperature, the greater part of the mixture melts, but a small quantity of a granular precipitate remains behind; this needs to be carefully separated, and consists of the hydrate $CdSO_4 + 7H_2O$. The moist compound appears to be stable at temperatures below +4°; at this temperature, however, it is slowly converted into the ordinary hydrate. The solubility of the new hydrate increases slowly from 44·45 per cent ($CdSO_4$) at −17° to 48·7 per cent. ($CdSO_4$) at −4·5°.

According to the authors, the ordinary hydrate does not effloresce on exposure to the air; they have, further, been unable to obtain the hydrate $2CdSO_4 + 5H_2O$ described by Rose (*Ann. Phys. Chem.*, **85**, 305), or the hydrate $CdSO_4 + 4H_2O$ described by Stromeyer. Ordinary crystallised cadmium sulphate readily effloresces, and, when powdered, loses all its water at 100°; this is due to small quantities of acid contained in the crystals; when quite free from acid, the crystals are extremely stable.

At 0°,

1 mol.	$MgSO_4 + 7H_2O$	requires	18·9	mols. H_2O for solution.
,,	$ZnSO_4 + 7H_2O$	,,	13·4	,, ,, ,, ,,
,,	$CdSO_4 + 7H_2O$	,,	3·4	,, ,, ,, ,,

That is, for this temperature the solubility increases with the atomic weight of the metal. J. J. S.

Earth contained in Monazite Sands. By Paul Schützenberger and O. Boudouard (*Compt. rend.*, 1897, **124**, 481—486).—The crystallised cerium sulphate prepared from monazite sands contains an oxide of higher molecular weight than that contained in cerium sulphate prepared from cerite.

After removal of didymium, lanthanum, and thorium, fractional crystallisation of the sulphate yields (1) a cerium with an atomic weight a little below 138, the solution of which is not precipitated by cupric oxide; (2) a cerium with an atomic weight of about 148, the sulphate of which is precipitated by cupric oxide, and also by sodium sulphate; (3) a cerium of atomic weight about 157, the sulphate of which is precipitated by cupric oxide, but not by sodium sulphate, and is characterised by a peculiar, gummy appearance which its aqueous solutions acquire during concentration. All three oxides yield yellow ceric salts which are converted on heating into white cerous salts, and they all behave in the same way with hydrogen peroxide in presence of

sodium hydroxide, and with ammonium oxalate. Their chlorides yield identical spark spectra.

A fraction soluble in normal ammonium oxalate solution and not precipitated by sodium sulphate does not give the cerium reactions but belongs to the thorium group. The sulphates of the metals allied to cerium, but of higher atomic weight, yield an intermediate oxide and not a dioxide when they are strongly heated, and this explains the differences observed between the analytical results obtained by precipitating the sulphuric acid with barium chloride on the one hand and by strongly heating the sulphate on the other (compare Abstr., 1896, ii, 475). C. H. B.

The Earths in Monazite Sands. By G. Urbain and E. Budischovsky (*Compt. rend.*, 1897, **124**, 618—621).—The authors have endeavoured to ascertain whether the earths from monazite sands contain a constituent with an atomic weight of about 100. The sands were those examined by Schützenberger and Boudouard, and the experiments were made with the fraction precipitable by sodium thiosulphate. The oxides were converted into nitrates, and afterwards into acetonylacetonates by precipitating with ammonia and adding acetylacetone. The acetylacetonates were fractionated by crystallisation from alcohol and from benzene. The fraction with atomic weight 95—97 gave by this method as extreme values 96 and 97. The fraction 98—102 gave extreme values 98 and 108, and the fraction 103—105 gave extreme values 97 and 112. It is noteworthy that the lowest numbers are considerably higher than the atomic weight of yttrium, and that the atomic weight of the mother liquor was in all cases higher than that of the crystals.

In determining the atomic weights, the nitrates were converted into sulphates and the latter were heated first in sulphur vapour and then at gradually increasing temperatures until the weight was constant, and finally the sulphates were converted into oxides by heating in a double platinum crucible (compare Schützenberger and Boudouard, preceding abstract). C. H. B.

Occurrence of Gallium in the Clay-ironstone of the Cleveland District of Yorkshire: Determination of Gallium in Blast-furnace Iron from Middlesbrough. By W. Noel Hartley and Hugh Ramage (*Proc. Roy. Soc.*, 1897, **60**, 393—407).—The blast furnace iron from Middlesbrough is found to contain 1 part of gallium in 33,000 parts of crude iron, which is more than in the richest source of this element hitherto known. The element is contained in the crude ore, and becomes concentrated in the metal.

The method employed in this examination was that of fractional precipitation by means of zinc, and also by ammonium acetate, with spectrographic analysis of the precipitates, supplemented by gravimetric determinations of the purified gallium sesquioxide.

A specimen of manganese ore examined was found to contain both gallium and indium, which is remarkable, as hitherto the latter has been found only in zinc blendes.

Clay ironstones from Middlesbrough, Whitby, Northamptonshire, and St. Andrews were all found to contain gallium. A. W. C.

Action of Iron on Solutions of Metallic Nitrates. By JEAN B. SENDERENS (*Bull. Soc. Chim.*, 1897, [iii], **15**, 691—700. Compare Abstr., 1897, ii, 171).—The author has studied the action of different kinds of iron (wrought iron piano wire, &c.) on dilute solutions of silver salts, and finds that unworked iron is far more active than worked iron, precipitating the silver readily from dilute solutions of the nitrate. This he attributes to a difference in the physical condition in the different samples of iron. M. W. T.

Ferric Alkali Salts of Sulphurous Acid. By KARL A. HOFMANN (*Zeit. anorg. Chem.*, 1897, **14**, 282—292).—The *salt* $Fe_2(SO_3)_4SO_4K_4 + 5H_2O$ is obtained by treating potassium iron heptanitrososulphonate, $KS_3Fe_4(NO)_7$, dissolved in alcohol with a solution of sodium hydrogen sulphite, and allowing the mixture to remain at the ordinary temperature for about 14 days. It forms a yellow, lustrous mass of microscopic needles, is insoluble in cold water, and when boiled with water is decomposed into ferric hydroxide and a soluble, ferrous salt. It dissolves immediately in 20 per cent. hydrochloric acid, and the solution gives a blue precipitate with potassium ferrocyanide, and only a brown coloration with potassium ferricyanide, whence the author concludes that the compound is a ferric salt. On boiling the hydrochloric acid solution, partial reduction of the ferric salt takes place.

The *salt* $Fe(SO_3)_2SO_4K_3$ is obtained by digesting the heptanitrososulphonate for about 1 month with sodium hydrogen sulphite at 4°. It crystallises in beautiful, lustrous, dark yellow leaflets, is almost insoluble in cold water, and behaves like the preceding salt when boiled with water or dilute acid.

The *salt* $FeSO_3SO_4K$, obtained by treating finely powdered iron ammonium alum with potassium hydrogen sulphite, crystallises in slender, double refracting needles. It is but sparingly soluble in cold water, and the solution contains ferric salt only. When heated for some time with water at 80—90°, ferrous sulphate and potassium sulphate are dissolved, and a yellow residue is obtained which is soluble with difficulty in dilute acids with evolution of sulphurous anhydride. It dissolves readily in cold, dilute hydrochloric acid, and the bright yellow solution gives a blue precipitate with potassium ferrocyanide, and only after boiling a blue with potassium ferricyanide.

The *salt* $FeSO_3SO_4NH_4 + H_2O$, obtained by treating ammonium alum with ammonium or sodium hydrogen sulphite, crystallises in slender, yellow needles, is only very slightly soluble in cold and hot water, and by prolonged boiling with water is converted into a red powder, with evolution of sulphurous anhydride. It is easily soluble in cold, dilute hydrochloric acid with evolution of sulphurous anhydride. When treated with ammonia or dilute alkali, it is decomposed, with formation of a brown, flocculent precipitate.

The *salt* $Fe(SO_3)_2SO_4Na_3 + 6H_2O$, is obtained by digesting sodium iron heptanitrososulphonate with sodium hydrogen sulphite for some days. It crystallises in lustrous, flat, yellow prisms, and is very similar to the corresponding potassium salt.

The *salt* $Fe_2SO_4(SO_3)_4H_2Na_2 + 2H_2O$ is obtained by dissolving freshly prepared ferric hydroxide in a concentrated solution of sodium hydrogen

sulphite and sulphurous acid. On evaporating the solution over sulphuric acid, a red, amorphous substance separates at first; but after this has been removed, a crystalline mixture of the salt together with the preceding salt is obtained. It can be separated by treating the mixed crystals with a solution of sodium hydrogen sulphite, and crystallises in bright olive-green needles. E. C. R.

Metallic Ammonium Compounds. II. By KARL A. HOFMANN (*Zeit. anorg. Chem.*, 1897, **14**, 263—281).—The reactions of the triammine salt, $C_2S_7Co_2(NH_3)_6$, already described (*Zeit. anorg. Chem.*, **11**, 379) have been examined to ascertain if more than 3 mols. of ammonia to 1 mol. of cobalt can be retained in the compounds.

The *compound* $C_2S_8Co_2(NH_3)_6O_3$ is obtained together with the salt, $CoS_2O_6(NH_3)_5$, when the above triammine salt is allowed to remain some months under 10 per cent. aqueous ammonia. The two compounds are separated by washing out the first salt, which crystallises in thin plates, with strong ammonia. The salt $CoS_2O_6(NH_3)_5$ is sparingly soluble in cold water, more easily in hot water, and when boiled suddenly deposits a bright brown precipitate. It dissolves to a reddish-yellow solution in warm soda solution, and on boiling deposits a dark brown precipitate. With dilute hydrochloric acid and barium chloride, it yields barium sulphate, cobaltous chloride, and sulphurous acid. The compound is, therefore, a cobaltisulphite ammonia salt. This is also proved by the formation of the salt $C_2S_7Co_2(NH_3)_6$ by boiling the ammonium cobaltous salt of cobaltisulphurous acid with ammonia.

The ammonia molecules of the salt $C_2S_7Co_2(NH_3)_6$ are only removed with difficulty by acids. Fuming hydrochloric acid at the ordinary temperature yields a compound of the formula $Co_2C_2ClS_{14}O_{10}H_{26}$ as a black, crystalline precipitate, and a blue solution is left. Acetic acid (60 per cent.), after many days at the ordinary temperature, yields the *compound* $(CS_3)_3Co_2S(NH_3)_2,C_2H_4O_2 + 4H_2O$, whereby hydrogen sulphide is liberated and much cobalt dissolved. This salt crystallises in small, lustrous, black scales. Acetic anhydride acts very slowly, and after 4 days a *compound*, $C_2S_8Co_25NH_3$, was obtained as a black, lustrous, crystalline powder.

The *compound* $C_2S_8Co_2(NH_3)_5H_2O$ is obtained by the action of diazobenzene nitrate on the triammine salt at 0° after 24 hours. It forms black, prismatic crystals, is slightly soluble in water, and gives an intense green coloration with dilute sodium hydroxide. With a large mass of diazobenzene nitrate and more prolonged action, more ammonia is eliminated, but the author was unable to isolate the compound formed.

Erdmann's cobalt triammine nitrite, $Co(NO_2)_3(NH_3)_3$, is obtained by treating the triammine salt suspended in water with nitrous oxide. Sulphur and carbon bisulphide are separated during the reaction. It crystallises from water in brownish-yellow needles.

The above results show that no ammonia is combined between the cobalt and sulphur, for, if this were the case, groups of the constitution $CoNH_3{\cdot}S{\cdot}NH_3Co$ or $Co{\cdot}NH_3{\cdot}S{\cdot}C$ would be formed, and the compound $C_2S_7Co_2(NH_3)_6$ should give the reactions of hydrogen sulphide or thiocarbonic acid.

The compound $C_2S_7Co_2(NH_3)_5 + 2H_2O$ is obtained by treating cobaltic hydroxide with 10 per cent. ammonia and carbon bisulphide and allowing the mixture to remain for some time below 10°. It crystallises in long, brownish-red needles, and decomposes gradually at the ordinary temperature with evolution of hydrogen sulphide.

The *compound* $CS_4CoH,3NH_3$ which is obtained by allowing the mixture employed for the preparation of the preceding compound to remain at the ordinary temperature for 4—5 days, crystallises in black prisms resembling hornblende, and is the compound from which the triammine salt, $C_2S_7Co_2(NH_3)_6$, is formed by the elimination of hydrogen sulphide. It dissolves in water with an intense yellow coloration, and in sodium hydroxide or ammonia to a greenish-yellow solution; neither of these solutions gives a coloration with sodium nitroferrocyanide, or a deposit of silver sulphide on a piece of metallic silver. It, therefore, does not contain ammonia between the cobalt and sulphur.

Cupric trithiocarbonate ammonia, CS_3CuNH_3, is obtained by treating a mixture of cuprous chloride and excess of ammonia (10 per cent.) with carbon bisulphide at 0°; after remaining 3 days, a separation of hair-like crystals takes place, and after another 2 days these are converted into the new salt. This crystallises in thick, green tablets having a metallic lustre, is only very sparingly soluble in strong ammonia, and gives a brown solution and a precipitate of brownish-black flocks with dilute sodium hydroxide. It is also obtained by the action of ammonia and carbon bisulphide on copper sulphate at 10°. When allowed to remain with 60 per cent. acetic acid for 4 days, it yields the *compound* CS_3Cu_2S, which crystallises in lustrous, bronze-coloured crystals.

The *compound* $C_2S_5Cu_3(NH_3)_6O_6$ is obtained by allowing a mixture of copper sulphate, 6 per cent. ammonia, and carbon bisulphide to remain at 0° for 4—5 weeks. It crystallises in black, monosymmetric tablets, dissolves easily in ammonia with a blue coloration, is insoluble in water, and is not decomposed when allowed to remain over sulphuric acid. Dilute sodium hydroxide has only a surface action on the compound; but it is completely decomposed by concentrated sodium hydroxide with formation of cupric hydroxide and sulphuric acid.

Zinc trithiocarbonate ammonia, $CS_3Zn(NH_3)_2$, is obtained by dissolving zinc sulphate in 10 per cent. ammonia, then adding excess of ammonia and after cooling at 5°, shaking the mixture with carbon bisulphide; it is a bright, salmon-coloured, crystalline powder. Cadmium sulphate forms a similar compound, which crystallises in lustrous, colourless plates, but decomposes with formation of cadmium sulphide when dried.

The thiocarbonates of platinum, iridium, and rhodium combine very easily with ammonia. The *salt* $Pt(NH_3)_2S_3C + H_2O$ is obtained from potassium platinous chloride, strong ammonia, and carbon bisulphide. It crystallises in long, red needles, is insoluble in cold water, ammonia, or sodium hydroxide, and gives up its water of crystallisation when allowed to remain in a vacuum over sulphuric acid. It gives no coloration with sodium nitroferrocyanide, nor a mercaptan nor methyl sulphide when boiled with methylic iodide. Under certain conditions,

which have not yet been determined, the *salt* $Pt_2Cl_2(NH_3)_4S_3C$ is formed, and crystallises in slender, red needles. The *salt* $C_2S_5PtNH_3$ is obtained from ammonium platinum chloride, ammonia, and carbon bisulphide; it crystallises in lustrous, black crystals, and is easily soluble in dilute sodium hydroxide. E. C. R.

Double Chromates. By JOSEF ZEHENTER (*Monatsh.*, 1897, **18**, 48—55).—If a solution of potassium dichromate (1 mol.) is treated with sodium carbonate (1 mol.), concentrated by heating, and finally allowed to crystallise in a vacuum over sulphuric acid, the following salts crystallise out in succession (the solubilities given represent the parts dissolved by 100 parts of water at 14°; the specific gravities were determined at 15°):—$3K_2CrO_4,Na_2CrO_4$, sp. gr. 2·719, solubility 64·2; $3K_2CrO_4,Na_2CrO_4 + \frac{1}{2}H_2O$, sp. gr. 2·575, solubility 66·4;

$$Na_2CrO_4 + 4H_2O;$$

the yields of these corresponded to 40, 30, and 20 per cent. respectively of the chromate taken.

By treating a solution of ammonium dichromate with potassium carbonate in molecular proportion, and precipitating with alcohol, the salt $3K_2CrO_4,2(NH_4)_2CrO_4$ is obtained; sp. gr. 2·403. By using sodium, instead of potassium, carbonate, the salt $NaNH_4CrO_4 + 2H_2O$ is obtained; sp. gr. 1·842. These two salts are decomposed by water or by heating.

From potassium dichromate and lithium carbonate, mixed in aqueous solution, the salt $K_2CrO_4,Li_2CrO_4 + \frac{1}{2}H_2O$, is obtained by evaporation in a vacuum; sp. gr. 2·539. C. F. B.

Stannic Chlorobromides. By J. ADOLPHE BESSON (*Compt. rend.*, 1897, **124**, 683—685).—The isolation of the stannic chlorobromides is difficult because they very readily decompose when distilled, even in a vacuum. They are produced by the action of dry hydrogen bromide on stannic chloride at 0°, or by the action of bromine on stannous chloride in presence of carbon tetrachloride, in which the products are soluble but the stannous chloride is not. The products are much more easily separated and obtained in a pure condition when prepared by the second method; the crude product is twice rapidly fractionated under very low pressure, and the fractions are further purified by fractional crystallisation at low temperatures.

Stannic chlorobromides are colourless liquids, which fume in moist air, with formation of crystalline hydrates, and dissolve in, and are decomposed by, water. They rapidly decompose into stannic chloride and stannic bromide when heated. The chlorobromide, $SnCl_3Br$, boils at about 50° under a pressure of 30 mm., and about 45° under a pressure of 20 mm., and melts at about −31°; sp. gr. = 2·51 at 13°. The chlorobromide, $SnCl_2Br_2$, boils at about 65° under a pressure of 30 mm., and melts at −20°; sp. gr. = 2·82 at 13°. The chlorobromide, $SnClBr_3$, boils at about 73° under a pressure of 30 mm., and melts at 1°; sp. gr. = 3·12 at 13°. C. H. B.

Action of Heat on Antimony Tetroxide. By HENRI BAUBIGNY (*Compt. rend.*, 1897, **124**, 560—562).—Antimony tetroxide, although stable at 800°, is decomposed at the melting point of silver, with forma-

tion of the trioxide. At the melting point of gold, the decomposition of the tetroxide and volatilisation of the trioxide are very rapid.

C. H. B.

Liquation of certain Alloys of Gold. By EDWARD MATTHEY (*Proc. Roy. Soc.*, 1896, **60**, 21—35).—On account of certain processes now employed for extracting gold from its ores, there has been introduced into this country a series of new alloys of gold and the base metals, principally lead and zinc, whose presence renders it impossible to estimate the true value of gold ingots by assaying in the ordinary way.

The author has found that samples taken from the opposite ends of the same ingot gave, on assaying, a fineness for gold varying between 439·35 and 662·45; and, in a second example, samples from the same end of an ingot varied between 332·5 and 652·0. In such cases, in order to obtain the true fineness, it becomes necessary to separate the gold in mass.

Numerous experiments were made to ascertain what effect the above-mentioned base metals exert when mixed with gold. When alloyed with lead alone, the gold seems to liquate towards the centre of the mass; with 25 per cent. of lead and zinc, the same phenomenon occurs, but here the result is complicated, as gravity sends the gold to the lower portion of the mass. If, however, silver is added in considerable quantity as well as lead and zinc, the alloy has a constant composition.

The cooling curves of these alloys also indicate that the presence of silver has a decided effect, as it acts as a solvent for both lead and zinc. The curve for an alloy of gold, copper, zinc, and lead shows that the mass solidifies as a whole at 635°, with decided breaks at 407° and 247°, temperatures which are evidently connected with the solidifying points of lead and zinc. If 10 per cent. of silver be added to the above alloy, only a slight break is noticed at 206°, and, on assaying, the mass is proved to have a fairly uniform composition. Provided not more than 30 per cent. of the base metals be present, silver will dissolve them with the above result.

A. W. C.

Action of Phosphorus on Gold. By A. GRANGER (*Compt. rend.*, 1897, **124**, 498—499).—Phosphorus can be distilled off finely divided gold without affecting it, but at about 400° its vapour attacks the metal, which swells up and becomes grey. At a dull red heat, the gold is not attacked by the phosphorus vapour, and hence the combination only takes place between narrow limits of temperature. If the tube is suddenly cooled whilst full of phosphorus vapour, a definite phosphide, Au_3P_4, is obtained; this is a very friable, grey compound, which is decomposed when heated in air, and is also slowly but completely decomposed when heated in a current of carbonic anhydride at the temperature at which it was formed; it is attacked by chlorine and aqua regia. Since phosphorus has no action on gold at high temperatures, a thin film of the metal forms a valuable protection to porcelain tubes, dishes, &c., which are exposed to phosphorus vapour at high temperatures.

C. H. B.

Mixed Platinohaloids. By ARTURO MIOLATI (*Zeit. anorg. Chem.*, 1897, **14**, 237—245).—The compound $K_2PtCl_4Br_2$, obtained by L.

Pitkin by adding potassium bromide to an aqueous solution of hydrogen platinochloride, is also obtained by treating potassium platinosochloride, K_2PtCl_4, with bromine, whereby a reaction takes place which is quite analogous to the addition of bromine or chlorine to the potassium platinonitrite or platinocyanide. The crude product, which on analysis gives numbers very nearly agreeing with those required by theory, can be recrystallised from warm water, and forms beautiful, orange-red, dichroic cubes; from the mother liquors, however, a less pure crystallisation is obtained. The analyses of several fractional separations show that the compound is very gradually decomposed. Determinations of the electric conductivity show that the decomposition in dilute, cold, aqueous solution is very gradual and approaches a maximum. The first determination observed at once after the complete solution of the salt is normal.

The salt K_2PtCl_6, as regards its electric conductivity, behaves as the potassium salt of the acid H_2PtCl_6. The corresponding bromine compound, K_2PtBr_6, on the other hand, behaves in a manner analogous to the salt $K_2PtCl_4Br_2$. A mixture of the two salts, K_2PtCl_6 and K_2PtBr_6, in the proportion corresponding with the salt $K_2PtCl_4Br_2$, gave numbers differing from those obtained for the salt $K_2PtCl_4Br_2$, but the differences were not sufficient to determine if the same or a different system is contained in the solutions. E. C. R.

Mineralogical Chemistry.

Mineral Tallow from Danby, Vermont. By L. E. SMOOT (*Amer. Chem. J.*, 1897, **19**, 233).—The substance is of a soft, smooth putty-like consistence, is nearly white, and on drying hardens to a pith-like mass. It is non-crystalline, and when heated in a closed tube, chars, giving off a small amount of alkaline vapours. Analysis gave:

	CaO.	MgO.	CO_2.	SiO_2.	H_2O lost in desiccator.	H_2O at 130°C.	Organic matter by difference.	N.	Total.
	7·63	0·04	6·04	0·52	84·37	1·01	0·39	—	100·00
Dried	52·19	0·27	41·31	3·57	—	—	2·66	(0·053)	100·00

A. W. C.

Periclase from Långban. By S. A. HJALMAR SJÖGREN (*Jahrb. f. Min.*, 1897, i, 11; from *Geol. Fören. i Stockholm Förh.*, 1895, **17**, 288—291).—Grains of periclase, which are surrounded by a shell of brucite, occur with hausmannite in a limestone poor in magnesium at Långban, Sweden. The green colour of the periclase is due to numerous enclosures arranged in zones parallel to the octahedral faces; these enclosures are mostly octahedral in form, but are sometimes elongated, and have their axes coinciding in direction with the axes of the periclase. As shown by the high content of manganous oxide, 8—9 per cent. in the periclase, these enclosures must be manganosite. In

the brucite shell, this manganosite is represented as brown and black hydrated oxides of manganese. The periclase is an original constituent of the limestone. L. J. S.

Analysis of Dolomitic Marble from Texas, Md. By GEORGE G. BUCK (*Amer. Chem. J.*, 1897, **19**, 234).—The marble has a faint yellow tint, with a sp. gr. $=2\cdot865$, and hardness $3\cdot5^{\circ}$. Its composition is:

CaO.	MgO.	FeO.	CO_2.	SiO_2.	Total.
31·58	19·64	0·14	47·55	1·27	100·18

which approximates fairly to that of a true dolomite. A. W. C.

Composition of Turquoise. By ADOLPHE CARNOT (*Bull. soc. fran. min.*, 1895, **18**, 119—123. Compare Abstr., 1894, ii, 355).—Turquoise with microcrystalline structure from a pegmatite at Burrow Mountains, Grant Co., New Mexico, gave the following results on analysis:

P_2O_5.	Al_2O_3.	CuO.	FeO.	CaO.	H_2O.	Quartz and clay.	Total.
28·29	34·32	7·41	0·91	7·93	18·24	2·73	99·83

Also traces of MnO, MgO, and fluorine. This agrees fairly closely with the formula previously given, namely, $P_2O_5(Al_2,Fe_3Ca_3Cu_3)O_3 + Al_2O_3 + 5H_2O$. L. J. S.

Copiapite and Botryogen from Falun. By S. A. HJALMAR SJÖGREN (*Jahrb. f. Min.*, 1897, i, 29; from *Geol. Fören. i Stockholm Förh.*, 1895, **17**, 306—312).—Copiapite occurs on botryogen at Falun, Sweden, as a fine-crystalline aggregate of sulphur, to citron-yellow colour. The minute, monosymmetric crystals are tabular parallel to (010) and have a rhombic outline; the optic axial plane is approximately parallel to (409) (not ($\bar{4}$09) as given by Linck), with the obtuse negative bisectrix perpendicular to (010). Analysis by Mauzelius gave the results under I; sp. gr. 2·08. Calculating FeO, MnO and ZnO with the MgO, this gives the formula $Fe_2(SO_4)_3 + 2Fe(OH)SO_4 + MgSO_4 + 21H_2O$. Taking this with other analyses, the author gives $20H_2O$ as being the most probable, but considers that it might vary slightly.

	SO_3.	Fe_2O_3.	FeO.	MnO.	ZnO.	MgO.	H_2O.	Insol.	Total.
I.	38·48	24·46	0·27	0·16	0·58	3·75	32·39	0·09	100·18
II.	37·78	19·60	0·38	0·44	2·50	7·31	31·39	0·21	99·61

The botryogen gave analysis II, by Mauzelius; sp. gr. 2·13; this agrees with an old analysis of Cleve's of the Falun mineral, and leads to the formula $MgFe'''(OH)(SO_4)_2 + 7H_2O$. L. J. S.

Tilasite or Fluor-adelite from Långban. By S. A. HJALMAR SJÖGREN (*Jahrb. f. Min.*, 1897, i, 25—26; from *Geol. Fören. i Stockholm Förh.*, 1895, **17**, 291—294).—Irregular grains of this new mineral are found with hausmannite, berzeliite and calcite in a grey limestone at Långban, Sweden. It is grey to pale violet in colour; the lustre on the fractured surfaces is greasy, and on the cleavage surfaces vitreous. Analysis by Mauzelius gave:

As_2O_5.	FeO.	MnO.	CaO.	MgO.	Na_2O.	H_2O.	Cl.	F.	Total less O for F.
50·91	0·14	0·16	25·32	18·22	0·29	0·28	0·02	8·24	100·11

The formula, $2CaO,MgO,MgF_2,As_2O_5$, is like that of adelite (Abstr., 1893, ii, 420), but with fluorine in place of OH. The optical examination of cleavage flakes shows the mineral to be anorthic.

L. J. S.

Mauzeliite, a New Antimonate from Jakobsberg, Sweden. By S. A. HJALMAR SJÖGREN (*Jahrb. f. Min.*, 1897, i, 26—27; from *Geol. Fören. i Stockholm Förh.*, 1895, **17**, 313—318).—Mauzeliite occurs, with a rose-red mineral which is probably svabite, in a calcite vein in a mixture of hausmannite, calcite, garnet, schefferite and manganophyllite at Jakobsberg, Sweden. The isometric crystals are 5—10 mm. across, of a brown colour, and show the forms {111}, {100}, {311}. Hardness 6—6·5; sp. gr. 5·11. Owing to cloudy enclosures, it is difficult to obtain pure material for analysis; the mean of the two analyses by Mauzelius is:

Sb_2O_5.	TiO_2.	PbO.	FeO.	MnO.	CaO.	MgO.	K_2O.	Na_2O.	H_2O.	F.
59·25	7·93	6·79	0·79	1·27	17·97	0·11	0·22	2·70	0·87	[3·63]

The fluorine could not be determined, and is given above as the difference; neglecting it, the formula is given as $Ti(SbO_4R^{II})_4 = 4R^{II}O,2Sb_2O_5,TiO_2$. The mineral is related to monimolite and atopite [and more closely to lewisite, Abstr., 1895, ii, 508]. L. J. S.

Analyses and Constitution of Vesuvian [Idocrase]. By S. A. HJALMAR SJÖGREN (*Jahrb. f. Min.*, 1897, i, 21—23; from *Geol. Fören. i Stockholm Förh.*, 1895, **17**, 267—278).—Under I is given the mean of two partial analyses by Mauzelius of pure, transparent mangan-idocrase from the Harstig mine, Pajsberg, Sweden; loss on ignition, 2·06 per cent.; a trace of copper or nickel is present; sp. gr. 3·45—3·433. II is the mean of three partial analyses by Mauzelius of green idocrase from Vaticha, near Nijni Tagilsk, in the Urals; traces of chromium and phosphoric acid are present.

	SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	MgO.	K_2O.	Na_2O.	H_2O.	F.	Total less O for F.
I.	35·38	—	10·19	8·14	—	4·81	34·18	4·39	0·47	0·46	1·46	1·99	100·64
II.	36·82	0·40	15·14	4·29	0·37	—	36·22	3·72	0·12	0·18	3·13	0·46	100·66

The mean of a series of the newer analyses of idocrase gives the ratio $R^{IV}O_2 : R^{III}{}_2O_3 : R^{II}O : (H_2O,F_2) = 6 : 1·72 : 7·30 : 0·98$. Taking 0·72 $R^{III}{}_2O_3$ and 0·72 (H_2O,F_2) to form the bivalent group $R^{III}(OH,F)$, and placing the remaining 0·26 (H_2O,F_2) with R^{II}, this ratio becomes $RO_2 : R_2O_3 : RO = 6 : 1 : 9$. This gives the formula $[Al(SiO_4)_3R^{II}{}_4]_2R^{II}$, in which $R^{II} = AlOH, AlF, FeOH, Ca \ldots H_2$; in the simplest case, it becomes $Al_2(SiO_4)_6Ca_9$. This formula is discussed in relation to the fusion and alteration products, and the mode of occurrence of idocrase (compare Abstr., 1895, ii, 511). L. J. S.

Alteration of Chondrodite, Tremolite and Dolomite into Serpentine at the Ko mine, Nordmark. By S. A. HJALMAR SJÖGREN (*Jahrb. f. Min.*, 1897, i, 19—21; from *Geol. Fören. i Stockholm Förh.*, 1895, **17**, 294—306).—The mineral occurrences at the Nordmark mines in Sweden, and particularly the Ko mine, are very similar to those at the Tilly Foster iron mine, New York, there being a similarity in the alteration products, as well as with the fresh minerals. The

chondrodite which occurs in the dolomite is more often altered to serpentine than that which occurs in the iron ore; with this alteration, the honey-yellow colour becomes greyish-yellow, and the lustre changes from vitreous to waxy, but the edges of the crystals remain sharp. The crystals are often surrounded by a detachable shell of altered material. Analysis I was made by Anderson on material which in thin sections showed, besides homogeneous serpentine material, an opaque substance considered to be a very fine mixture of calcite and serpentine. Analysis II, by Mauzelius, is of more altered, and nearly homogeneous, material; at 115—120°, it lost 3·2 per cent. Deducting CO_2 and the corresponding amount of CaO to form $CaCO_3$, only II approaches to serpentine in composition. Constitutional formulæ, illustrating the processes of alteration, are given:

	SiO_2.	CO_2.	Fe_2O_3.	FeO.	MnO.	CaO.	MgO.	H_2O.	F.	Total less O for F.
I.	31·19	7·08	—	2·37	0·74	15·98	29·60	9·46	4·33	98·72
II.	42·07	trace	1·26	4·31	3·36	0·76	34·57	12·89	0·91	99·75
III.	24·83	18·07	—	1·53	0·72	23·44	23·93	6·65	1·95	100·30
IV.	42·30	—	1·50	1·66	1·51	0·22	37·75	14·14	1·15	99·75

Tremolite is frequently altered into serpentine; the crystal form remains, but the transparency and vitreous lustre are lost. The altered part is sharply separated from the unaltered, and usually consists of pure, fibrous serpentine. Analysis by Mauzelius gave III; at 120°, there is a loss of 2·16 per cent. After deducting $CaCO_3$, the remainder has the composition of serpentine.

Dolomite is also often altered into serpentine, and this frequently forms the matrix of the altered chondrodite and tremolite. It is greyish-green, has a greasy lustre, and a conchoidal to splintery fracture; in thin sections, it is seen to be structureless. Analysis by Mauzelius gave IV; at 120°, there is a loss of 4·5 per cent.; this corresponds with 2 mols. of serpentine + 1 mol. cerolite.

Chondrodite is sometimes altered to dolomite (or calcite). In these alterations, there has then been both serpentinisation and carbonatisation, and fluorine seems to have played a part. L. J. S.

Physical-chemical Investigation of Desmine [Stilbite]. By FRIEDRICH RINNE (*Jahrb. f. Min.*, 1897, i, 41—60).—When stilbite ($CaAl_2Si_6O_{16} + 6H_2O$) is placed in concentrated sulphuric acid, the loss of water is accompanied by a progressive change in the optical characters of the crystals; the optic axes vary their positions, passing through uniaxial positions four times. The same change takes place when the crystals are heated, and from the powdered mineral the following percentages of water are lost:

125°	150°	185°	240°	260°	275°	300°	325°	350°	375°	400°
4·27	8·09	10·32	12·10	13·21	13·86	14·69	15·28	15·49	16·05	16·53 p.ct.

Over sulphuric acid, and at 100° (1·5 per cent.) small amounts of hygroscopic water are lost; on ignition, there is a loss of 18·40 per cent. These changes are gradual, but the following stages can be distinguished:

Temperature.	$CaAl_2Si_6O_{16}$ +	Uniaxial on	System.
125°	$5H_2O$	($\bar{2}01$)	Monosymmetric.
150	$4H_2O$	(010)	,,
185	$3H_2O$	(001)	,,
250	$2H_2O$	($\bar{2}01$)	Passage to orthorhombic.
350	H_2O	—	Orthorhombic.
Ignition	—	—	Amorphous.

The name *metadesmine* is given to these dehydrated forms. These changes are analogous to those which take place in heulandite. By the action of dilute acids, birefringent forms of silica are produced as in heulandite (Abstr., 1896, ii, 368). L. J. S.

Analyses and Constitution of Axinite. By S. A. HJALMAR SJÖGREN (*Jahrb. f. Min.*, 1897, i, 23—24; from *Geol. Fören. i Stockholm Förh.*, 1895, **17**, 279—288).—The following analyses are given. I, Brown axinite from Nordmark; sp. gr. 3·3. II, ditto. III, Grey axinite from Nordmark; sp. gr. 3·28. IV, Axinite from Dannemora; sp. gr. 3·3. Analysis II is by A. Cleve, the others by Mauzelius:

	SiO_2.	B_2O_3.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	MgO.	K_2O.	Na_2O.	H_2O.	F.	Total, less O for F.
I.	42·40	4·88	17·26	1·33	4·27	6·97	19·53	1·30	0·21	0·25	1·90	trace	100·30
II.	42·55	4·20	16·37	3·79	4·06	7·69	19·28	1·02	—	0·10	1·33	—	100·39
III.	42·40	4·71	17·39	0·59	4·89	6·16	19·57	1·69	0·25	0·24	1·64	0·22	99·66
IV.	41·96	4·61	17·69	0·81	3·61	8·51	19·71	0·97	not det.		1·93	1·11	100·44

The Al_2O_3 of I and III includes some TiO_2; the H_2O in II is too low. Here $B:Si = 1:5$ (really $1:5·03$, $1:5·85$, $1:5·21$, and $1:5·29$ respectively), $R:Si = 1:2$, and $Si:O = 1:4$, when $R = (Al_{\frac{2}{3}},Fe,Ca\ldots H_2)$; from this follows the formula $BAl(SiO_4)_5R''_7$. Preference is, however, given to the basic metasilicate formula, $Al(BO_2)(SiO_3)_5R''_4$, as powdered axinite has an alkaline reaction; in this, boron being a negative element, BO_2 is considered as an acid radicle. Several of the more certain published analyses also give in the mean the ratio $B:Al:SiO_3:(R'' + 2R''OH + 2AlO) = 1:1:5:4$. L. J. S.

Edingtonite from Böhlet, Sweden. By OTTO NORDENSKIÖLD (*Bull. soc. fran. min.*, 1895, **18**, 396—398; and *Geol. Fören. i Stockholm Förh.*, 1895, **17**, 597—600).—This zeolite, previously only known from Old Kilpatrick, in Dumbartonshire, was determined by Haidinger to be tetragonal and hemihedral. Examination of large crystals of a new find at the manganese mines at Böhlet, in Vestergötland, shows the mineral to be orthorhombic and hemihedral, with $a:b:c = 0·9872:1:0·6733$. There are perfect cleavages parallel to $m(110)$, ($mm' = 89° 16'$), and one less distinct parallel to $c(001)$. The plane of the optic axes is $b(010)$, and the acute negative bisectrix is perpendicular to $c(001)$; $2V_{Na} = 52° 55'$; sp. gr. 2·776. Detailed crystallographic and optical determinations are given. The axial ratios are compared with those of natrolite and scolecite. L. J. S.

Analysis of a Variety of Ilmenite. By GEORGE M. PEEK (*Amer. Chem. J.*, 1897, **19**, 232).—The specimen examined was from

Bedford Co., Va. It occurs enclosed in veins of quartz, it cleaves well in one direction, and less readily in a second at an angle of 45°. Sp. gr. = 4·699; hardness 5·25. It is not magnetic. The crystals are probably tetragonal. Analyses gave

TiO_2.	FeO.	MgO.	SiO_2.	Total.
63·31	35·99	0·82	1·25	101·37

This approximates with the formula $Fe_2Ti_3O_8$. A. W. C.

Synthetical Studies. By CORNELIUS DOELTER (*Jahrb. f. Min.*, 1897, i, 1—26)—Various minerals have been fused alone or with chlorides, fluorides, &c., and the fused mass allowed to cool slowly; the minerals thus formed in the glassy products vary considerably, and depend probably on the temperature at which solidification takes place, the action of the fluxes being mainly in lowering the temperature. At higher temperatures, olivine, leucite, augite, scapolite, and nephelite are formed, at lower temperatures, hornblende, mica, garnet, albite, and orthoclase. As a rule, orthosilicates seem to be the most stable, whilst metasilicates are easily altered into orthosilicates.

Micas when fused alone, usually give leucite and nephelite, but meroxene gives augite, spinel and scapolite. Tourmaline gives olivine and spinel, and, with calcium chloride and sodium fluoride, also melilite. Axinite and epidote give lime-augite and anorthite; epidote with fluorides gives anorthite, meionite, garnet, olivine, &c., and sometimes epidote recrystallises. Zoisite with chlorides gives garnet, olivine and anorthite. Hornblende gives augite, olivine, &c., and attempts to prepare hornblende by fusion usually result in these minerals being formed; but when the temperature is lowered to 500—700° by the addition of borax, &c., hornblende crystals can be produced by the fusion of powdered hornblende or of a mixture of the necessary oxides. Minerals of the scapolite group are frequently formed when various minerals and rocks are fused; meionite is obtained in good crystals by fusing a mixture having the composition of this mineral. Acmite is formed with magnetite and hæmatite by fusing $Na_2Fe_2Si_4O_{12}$. A mixture of $Al_2O_3 + 2SiO_2$ fused with fluorides gives mica, nephelite, leucite, scapolite, and felspars; the results of fusing various other mixtures are also described in detail. The significance of these and many other similar reactions are discussed in connection with the genesis of igneous rocks.

L. J. S.

Analyses of Infusorial Earth. By F. W. SMITHER (*Amer. Chem. J.*, 1897, **19**, 235—236).—Analyses of three samples of infusorial earth, consisting almost entirely of shells, gave the following results:

	SiO_2 amorphous.	SiO_2 cryst.	TiO_2.	Fe_2O_3.	Al_2O_3.	MgO.	CaO.	OH_2 at 100°.	Loss on ignition.	Total.
Rappahannock	65·83	14·65	0·40	2·34	4·17	0·71	trace	4·13	7·50	99·73
Richmond......	51·67	23·56	0·64	2·79	10·25	0·69	0·27	4·73	5·45	100·05
Patuxent.........	48·58	35·23	0·60	1·20	5·20	—	0·25	5·09	4·22	100·37

A. W. C.

An Alum Water from Lee Co., Virginia. By L. E. SMOOT (*Amer. Chem. J.*, 1897, **19**, 234).—The water is odourless and colour-

less, with a decided acid reaction and strong taste of alum. The temperature of the spring is 70° F. composition:

	Al_2O_3.	Fe_2O_3.	Na_2O.	SO_3.	N_2O_5.	SiO_2.	Total.
Grams per litre	0·891	0·120	0·060	2·530	0·006	0·108	3·715

A. W. C.

Physiological Chemistry.

Digestibility of Cacao-butter and of Butter from Cow's Milk. By BOUROT and FERDINAND JEAN (*Compt. rend.*, 1896, **123**, 587—590).—Cacao butter is used as a food in many countries, and the present experiments show that it has a high nutritive value; ordinary butter was digested to the extent of 95·8, and cacao-butter to that of 98 per cent.; in both cases, therefore, a very small residue of fat was found in the fæces. W. D. H.

Effect of Fresh Thyroid and Iodothyrin on Metabolism. By FRITZ VOIT (*Zeit. Biol.*, 1897, **35**, 116—154).—The experiments were carried out on dogs in the usual way; the ingesta and egesta were analysed, both while the animal was taking normal diet and diet to which was added either fresh thyroid or iodothyrin. The result produced by either addition was the same, namely, an increase in the quantity of urine and excretion of nitrogen, a deficit in nitrogenous equilibrium, a loss of weight, a loss of fat, and an increase of excretion of carbonic anhydride. If the animals were in a state of inanition, these results were more marked. A review of previous work on the subject is given. W. D. H.

Source of Muscular Energy. By J. B. AUGUSTE CHAUVEAU (*Compt. rend.*, 1896, **122**, 1303—1309).—By a comparison of the work and heat produced by contracting muscles, with the products of combustion, and the carbohydrate nutriment supplied to them, it is considered that the nature of the transformation of potential into actual energy is, as Lavoisier taught, combustion pure and simple.
W. D. H.

Source of Muscular Energy. By J. B. AUGUSTE CHAUVEAU and F. LAULANIÉ (*Compt. rend.*, 1896, **122**, 1244—1250).—Experiments were made on dogs and rabbits; the nutrition was either *nil* or abundance of carbohydrates. The muscles were excited to activity electrically, and the respiratory quotient determined before, during, and after, muscular work. The source of muscular energy is regarded as being always carbohydrate in nature, either from the store of glycogen in the body, or indirectly by a transformation of fat, or from the carbohydrate furnished directly to the muscles during absorption of food. W. D. H.

Coagulating and Toxic Properties of the Liver. By ALBERT MAIRET and VIRES (*Compt. rend.*, 1896, **123**, 1076—1078).—An aqueous extract of rabbit's liver was injected intravenously into other

rabbits, and found in certain doses to cause death; the blood was found to be coagulated in the heart and veins. By heating the extract, a coagulum is obtained; this contains the substance which produces the intravascular clotting; the filtrate is, however, still toxic, although it does not coagulate the blood. W. D. H.

The Active Physiological Substances of the Suprarenal Gland. By B. MOORE (*J. Physiol.*, 1897, **21**, 382—389).—The active substance of the medulla is not catechol, or a derivative of catechol as Frænkel considers; neither is it identical with the chromogen originally described by Vulpian, for alcohol destroys the activity of the substance without affecting the reactions of the chromogen. It is suggested that the active substance is a pyridine derivative, possibly piperidine. The last named alkaloid certainly produces a great rise of blood pressure (see also Tunnicliffe, *Centr. Physiol.*, March 8th, 1897).

W. D. H.

Thrombosin. By C. D. CRAMER (*Zeit. physiol. Chem.*, 1897, **23**, 74—86).—Schäfer and Hammarsten have previously expressed the opinion that Lilienfeld's thrombosin is nothing else but fibrinogen. The elementary analysis given in the present communication confirms this view. W. D. H.

The Reaction of the Intestine in Relationship to Intestinal Digestion. By B. MOORE and D. P. ROCKWOOD (*J. Physiol.*, 1897, **21**, 373—381).—Under normal conditions, the intestinal contents are not acid throughout, although in a few exceptional cases an undue amount of bacterial action may produce this result. The alkalinity is greater in herbivora than in carnivora, but in carnivora may be made to resemble that of herbivora by diet, for instance, feeding a dog on bread and water.

Fats induce an acid reaction throughout the greater part of the dog's intestine, but in rats and guinea pigs the contents remain alkaline. This is due to weak organic acids, which do not affect methyl-orange, but affect litmus.

Proteid (lean horseflesh) gives an acid reaction in the upper part of the intestine, and a faint alkaline reaction in the lower part in dog and cat, but in rats there is an alkaline reaction throughout.

The experiments indicate that, contrary to current theory, very little bacterial decomposition of carbohydrates takes place in the small intestine. Acidity begins in the cæcum. It is regarded as probable that the human intestine lies intermediate between that of carnivora and of herbivora. W. D. H.

Comparison of the Diffusion into Serum, and Absorption by the Intestine, of Peptone and Glucose. By E. WAYMOUTH REID (*J. Physiol.*, 1897, **21**, 408—425).—The diffusibility of peptone through parchment paper into serum is greater, and that of glucose slightly less, than into water. The absorption of glucose and peptone by the gut in different animals is not proportional to the extent of the absorbing surface.

The ratio of diffusion of glucose and of Grübler's peptone, through parchment paper into serum holding 0·1 per cent. of glucose in solution,

is not the ratio of the absorptions of these substances by the intestinal mucous membrane. The latter is slightly less permeable by glucose than by Grübler's peptone, whilst in the case of parchment paper it is the reverse.

The relation of diffusion of Grübler's and dialysed Witte's peptone through parchment paper into serum is also not the ratio of the absorptions of these substances in the gut. The latter is about equally permeable by both substances, while parchment paper is more permeable to Grübler's than to Witte's preparation. W. D. H.

Permeability of Membranes for Putrefaction Processes. By HANS HENSEN (*Zeit. Biol.*, 1897, **35**, 101—115).—Bacteria can pass through the membranes (artificial and natural) used in diffusion experiments, even when they will not permit the passage of such substances as hæmoglobin. A membrane without such a disadvantage is still to be found. W. D. H.

The Chemical Changes within the Organism of a Normal Animal. By MAURICE KAUFMANN (*Bied. Centr.*, 1897, **26**, 25—26; from *Arch. Physiol.*, [v], **8**, 329—341).—In a dog fed with milk containing much cane-sugar, there was abundant deposition of fat, produced by the partial oxidation of proteids. The heat evolved amounted to one-eighth to one-fourth of the total amount of heat which the dog developed; most of the heat produced arose from the complete oxidation of the sugar in the blood. In the case of carnivorous animals, only a very slight amount of sugar is converted into fat, whilst in vegetarians and animals which consume mixed food, sugar has a direct and essential share in producing fat. A portion of the sugar is deposited in the liver and muscles as glycogen.

When much proteid is consumed, it is decomposed into fat, carbonic anhydride, urea, and water, the fat being partly deposited and partly converted, first into sugar, then into carbonic anhydride. Most of the heat results from the primary oxidation of the proteids.

Fat, when consumed in conjunction with plenty of proteid or carbohydrate, is completely or partly deposited. It is, however, partly oxidised when the supply of carbohydrates in the body is diminished, as after 24 hours' fasting.

When food is withheld, the animal lives on reserve carbohydrates. Although the amount reserved is small, glycogen is found in the muscles after 10—15 days' fasting. The proteids and the fat are first converted into sugar, then burnt. There are three periods of hunger: first the supply of carbohydrates is diminished, then the loss of carbohydrates is made up from proteids and fat, the co-efficient of respiration sinking to 0·66. In the third period, sugar is produced in exactly the same proportion as it is burnt, that is to say, the animal lives on the decomposition of proteids and fat. The co-efficient of respiration is at this time 0·74. The proteids furnish one-sixth of the total heat at the beginning, and one-third at the end, of the period of fasting.

N. H. J. M.

Decomposition of Proteid in the Human Organism. By EYVIND BÖDTKER (*Bied. Centr.*, 1897, **26**, 130; from *Centr. Med. Wiss.*,

34, 354).—In healthy adults, the urea excreted contained from 88·44 to 91·39 per cent. of the total nitrogen. The uric acid nitrogen amounted, on the average, to 1·5 per cent. of the total nitrogen. There is no constant relation between the percentage of nitrogen as uric acid, and as ammonia, and the total nitrogen. The average amount of ammoniacal nitrogen is 4 per cent. of the total. In children, the relation of urea and uric acid is about the same as in adults, but the ammoniacal nitrogen is usually higher (4 up to 9 per cent.). In slight cases of diabetes, the urea nitrogen is about 87 per cent., whilst the nitrogen as ammonia rises to over 13 per cent. The effect of other diseases on the form in which nitrogen is excreted was investigated.

N. H. J. M.

Transformation of Fat into Carbohydrate in the Organism. By J. B. AUGUSTE CHAUVEAU (*Compt. rend.*, 1896, **122**, 1098—1103).—In a starving animal, and during hibernation, the sugar which still persists in the blood must originate from either fat or proteid. Further, in hibernation, Regnault and Reiset showed that the respiratory quotient was very low, and the great excess of oxygen retained over carbonic anhydride given out leads to an actual increase of weight of the animal, but it loses its fat.

W. D. H.

Formation of Nuclein in Mammals. By RICHARD BURIÁN and HEINRICH SCHUR (*Zeit. physiol. Chem.*, 1897, **23**, 55—73).—In connection with the probable origin of nuclein in the body, the question specially investigated in the present research is whether the administration of xanthine bases leads to the formation of nuclein. The experiments recorded on rabbits and dogs show that the bases can be formed in the body from other nitrogenous material, but mainly negative results were obtained relating to the special point investigated.

W. D. H.

Fat Estimation. By FR. N. SCHULZ (*Pflüger's Archiv.*, 1897, **66**, 145—166).—Dormeyer's digestion method of estimating fat in muscle can be applied with advantage to other tissues and organs. Mere inspection is untrustworthy in the formation of an opinion as to the amount of fat in a starving animal. An extended period of inanition is required to make an animal fat free, or at least to bring it to the lowest limit of the percentage of fat observed. The amount of nitrogen of the different dry, fat-free organs is about the same. The relative amount of cholesterol rises in the organs; this may be because this substance is not altered by hunger as fat is.

W. D. H.

"Oxidation-ferments" of the Tissues. By ERNST L. SALKOWSKI and KATSUSABURŌ YAMAGIWA (*Virchow's Archiv.*, 1897, **147**, 1—23).—It was shown by Jaquet (*Arch. exp. Path. Pharm.*, **29**, 386) that the tissues have the power of oxidising at the body temperature such substances as benzylic alcohol and salicylaldehyde. This does not depend on the life of the protoplasm, but on the presence of a soluble ferment. which is destroyed by boiling, and by the prolonged action of alcohol. The present research shows that the blood has the same power, Extracts of various organs act, however, with different degrees of oxidising power, as estimated by the amount of salicylic acid formed

from salicylaldehyde. The liver is the most powerful; and if its power is put at 100, the power of the spleen is 80·4; of the kidneys, 15·5; of the pancreas, 2·0; and of the muscles, 1·0. W. D. H.

Non-putrescibility of Blood rendered Incoagulable by Leech-extract. By Bosc and Delezenne (*Compt. rend.*, 1896, **123**, 465—467, 500—503).—Shed blood, which is kept fluid by a previous intravenous injection of leech-extract, does not putrefy readily. This is not due to the presence of any antiseptic substance in the extract, nor to an increased phagocytic action of the leucocytes, for the blood remains unputrefied after the death of the white corpuscles. The extract perhaps provokes such secretions from the corpuscles as increase the bactericidal power of the blood. In fact, the injection of leech-extract confers immunity on the animals to certain experimental infections. W. D. H.

Pigments of Decapod Crustacea. By M. I. Newbiggin (*J. Physiol.*, 1897, **21**, 237—257).—The animals investigated were the common lobster, *Nephrops*, the Norway lobster, and *Astacus nobilis*, the red-clawed crayfish.

In their shells, hypodermis, and ova there is a red lipochrome pigment. In shell and hypodermis this is either accompanied by a small amount of a yellow pigment, or more probably the red pigment is unstable and is converted by certain reagents, especially under the influence of heat, into a yellow pigment. The yellow pigment is identical with that occurring in the digestive gland, and is in part eliminated with the fæces.

The red lipochrome readily forms combinations with alkalis and alkaline earths; the compounds so formed are orange, and almost insoluble in alcohol. As the undecalcified shell of *Nephrops* is orange and yields like pigment to cold alcohol, whilst the decalcified shell is pink and yields its pigment readily to alcohol, it is probable that, in a shell, the pigment is present in combination with lime. The deep sea crustacea and the more delicate surface forms have but little lime in their cuticle, and are deep red.

The red lipochrome unites also with an organic base apparently derived from the muscle, and thus gives rise to the blue pigment of these animals.

The yellow hepatochrome of the liver appears to be the central pigment of the group; this may become modified to form the red lipochrome of the shell, or the orange pigment of the shell if it unites with lime. If the red lipochrome unites with the organic base, the blue is formed, and a mixture of the blue with unaltered yellow gives rise to green. W. D. H.

Non-occurrence of Argon in the Colouring Matter of the Blood. By J. Zaleski (*Ber.*, 1897, **30**, 965—969).—The gas obtained on burning the colouring matter of the blood with copper oxide was freed from nitrogen by means of magnesium or lithium, a modified form of the Schlœsing apparatus being used for the purpose; the residual gas, however, in no case showed the characteristic spectra of argon. J. F. T.

Biological Relation of Chlorophyll and Hæmoglobin. By MARCELLUS NENCKI (*Ber.*, 29, 2877—2883).—Schunck and Marchlewski (*Annalen*, 290, 306) have shown that *phylloporphyrin*, $C_{16}H_{18}N_2O$, a substance obtained from chlorophyll, is nearly related to hæmatoporphyrin, $C_{16}H_{18}N_2O_3$; hæmin and phyllotaonin are also similar and form similar compounds, this similarity extending to spectroscopic appearances. It appears, therefore, that the basis of blood pigment and leaf pigment is the same; in view of the Darwinian hypothesis, and the essential unity of living things, such a discovery is of value. The rest of the paper deals with the biological importance of the question, and other examples of the universal application of certain chemico-biological laws are taken from different parts of the animal and vegetable kingdom. W. D. H.

Composition and Nutritive Value of Sardines Preserved in Oil. By DOMENICO MARTELLI (*Staz. Sper. Agrar.*, 1895, 28, 225—235). —The following percentage results were obtained with sardines from (1) Sicily, (2) Tunis, and (3) Sardinia:

	Water.	Fat.	Nitrogen as Proteids.	NH_3.	Ash.	CaO.	MgO.	P_2O_5.	SO_3.	Cl.
1.	50·16	12·68	4·302	0·168	7·51	0·09	0·19	0·61	0·03	3·77
2.	50·36	13·07	4·075	0·193	7·85	0·14	0·21	0·58	0·02	4·08
3.	40·66	23·75	3·836	0·252	8·98	0·07	0·20	0·53	0·01	4·73

A part of the organic nitrogen (given as "nitrogen as proteids") is probably present in the form of amides or amido-acids.

Calculating the nutritive value of the fish by König's method, taking the value of the proteids and fat respectively as 5 and 3 times that of carbohydrates, 1 kilogram of each of the three samples is found to contain the following numbers of units of nutritive value: (1) 1725, (2) 1666, and (3) 1900. N. H. J. M.

Formation of Urea by Oxidation. By FRANZ HOFMEISTER (*Chem. Centr.*, 1896, ii, 389—390; from *Arch. exp. Path. Pharm.*, 37, 426—444).—With the exception of Béchamp's unrecognised attempts, the formation of urea from albumin or other nitrogenous substances has not been proved. Schultzen and Nencki showed that the nitrogen of amido-acids is excreted almost entirely as urea, and Knieriem proved that even ammonium salts are changed into urea in the animal organism. The most general view, therefore, of the origin of urea is that the final products of oxidation, carbonic anhydride, and ammonia form urea with elimination of water. Drechsel has shown that, by hydrolysis, only a small portion of the nitrogen of albumin is eliminated as urea.

By oxidation of a great variety of substances with potassium permanganate, the author has obtained urea, often even in considerable quantity. The substance was oxidised in aqueous solution with addition of ammonia and ammonium sulphate, by means of a quantity of potassium permanganate nearly sufficient to convert it into carbonic anhydride, water, and urea. Decolorisation took place in times varying from a quarter of an hour to several days. The liquid was then filtered, the filtrate evaporated almost to dryness at 40—50°, and the

crystalline mass digested 10—12 hours with 96 per cent. alcohol. The filtrate was evaporated, and to the residue dissolved in alcohol half its volume of ether was added and the whole then filtered and evaporated. The presence of urea in the residue was proved by preparation of the nitrate and its microscopical examination, or, when in sufficient quantity, by determination of the melting point and estimation of the nitrogen.

Urea was proved to have been formed in the cases of hydrocyanic acid, thiocyanic acid, formamide, glycocine (3 grams of urea nitrate from 10 grams of glycocine), oxamic acid (0·7 gram of nitrate from 10 grams of acid), aspartic acid, asparagine, leucine (0·2 gram nitrate from 5 grams of leucine), gelatin, egg-albumin (2 grams of nitrate from 39 grams of albumin), methylic alcohol, ethylene glycol, glycollic acid, acetone, lactic acid, malic acid, tartaric acid (0·7 gram of nitrate from 20 grams of acid), and pyrogallol. No urea was formed from ethylamine, acetonitrile, acetamide, oxamide, succinamide, formaldehyde, formic acid, carbonic acid (ammonium carbonate containing carbamate), ethylic alcohol, acetaldehyde, acetic acid, glyoxal, propionic acid, malonic acid, glyceric acid, butyric acid, succinic acid, or grape sugar.

This synthesis of urea depends on the union of NH_2- and $CO-$ groups, hence compounds containing no nitrogen may form urea by the help of ammonia. The experiments show that the groups $CH_3\cdot C\equiv$ and $\equiv C\cdot COOH$ cannot yield urea, whilst $-CH\cdot NH_2, -COOH$, and $-CH\cdot OH, -COOH$ very easily form it, and that the groups $-CN$ and $-CH_2\cdot OH$ can furnish the CO groups necessary for the formation of urea only when present in the simplest carbon compounds, such as formamide, oxamic acid, hydrocyanic acid, methylic alcohol, or ethylene glycol.

The substances which, on oxidation with permanganate, did not form urea, such as acetamide and oxamide, are also unchanged in the animal organism, whereas oxamic acid which yielded urea is also oxidised to urea in the body without previous formation of oxalate. It is still uncertain, however, as to whether this natural synthesis of urea is one of oxidation and elimination of water, but such an assumption does away with the necessity of attributing a special function to the liver, as this organ is found to be especially capable of oxidising fatty substances. The author's observation that the liver contains no cyanic acid is opposed to the view that the formation of urea is analogous to its production from ammonium cyanate. E. W. W.

Excretion of Nitrogen by the Intestine. By JIRO TSUBOI (*Zeit. Biol.*, 1897, **35**, 68—93).—Consideration of results of previous workers, and the present examination of the fæces in dogs, show that the amount of nitrogen that leaves the body by the intestine is by no means negligible, and varies with diet. Less proteid is assimilated when it is mixed with fat than when it is mixed with starch. This fact must be taken into consideration in all studies on metabolic phenomena, even if the products of nitrogenous metabolism in the fæces are scanty. W. D. H.

The Fat of Ovarian Dermoid Cysts. By ERNST LUDWIG (*Zeit. physiol. Chem.*, 1897, **23**, 38—39).—From fat obtained from the interior of numerous dermoid cysts of the ovary, cetylic alcohol was

separated, and also a new oily substance, similar in many points to cholesterol. W. D. H.

The Fat of Ovarian Dermoid Cysts. By RICHARD VON ZEYNEK (*Zeit. physiol. Chem.*, 1897, **23**, 40—54).—A fuller investigation of the cholesterol-like substance alluded to in the preceding abstract. By fractional distillation, it was separated into five fractions differing in their solubilities, optical activity, and percentage composition. Attempts to make crystalline compounds, however, failed. No further conclusion than that the substance has some resemblance to cholesterol is arrived at. W. D. H.

A Remarkable Case of Alcaptonuria: Estimation of Alcapton (Homogentisic Acid). By GEORGES DENIGÈS (*J. Pharm.*, 1897, [vi], **5**, 50—54).—In a case of facial and sciatic neuralgia, it was found that, although polarimetric examination of the urine gave negative results, and the urine did not ferment in presence of yeast, the quantity of glucose indicated by Fehling's test was considerable.

In 1859, Bœdecker separated from urine of a similar nature, a substance, alcapton, which was shown by Wolkow and Baumann to be a homogentisic acid, $C_6H_3(OH)_2 \cdot CH_2 \cdot COOH$ (Abstr., 1891, ii, 1128).

The author succeeded in separating a quantity of this substance from the sample of urine in question. He further succeeded in showing that the quantity secreted is increased under meat diet, and is roughly proportional to the quantity of urea present. This confirms Baumann's theory that alcapton is formed by the breaking down of tyrosine.

Alcapton may be estimated in the following manner: 10 c.c. of filtered urine, 10 c.c. of ammonia solution, and 20 c.c. of decinormal silver nitrate solution are placed together in a flask for 5 minutes. Five drops of calcium chloride solution and 0·5 c.c. of ammonium carbonate solution are added; the solution is made up to 50 c.c., and filtered. The silver is estimated in half the filtrate. One molecule of alcapton, $C_8H_8O_4$, reduces 4 atoms of silver. M. W. T.

Osmotic Properties of Cells in their Bearing on Toxicology and Pharmacy. By ERNST OVERTON (*Zeit. physikal. Chem.*, 1897, **22**, 189—209).—The author considers more especially the peculiar selective influence of some classes of poisons and medicines, as a consequence of which only one class of cells is especially affected, the remainder being either not affected or only indirectly. As in some cases the gain or loss of a compound by the cell protoplasm is not a purely osmotic process, the local action could be explained by the assumption that the poison, &c., only enters the particular cells which exhibit the alteration of function. This, however, does not appear to be the case in the majority of cases, and many toxic compounds including the anæsthetics, hypnotics, and antipyretics readily pass through both plant and animal membranes, so that in their case the passage is solely osmotic. The local action is hence most probably due to the fact that the functional activity of the one class of cells is materially influenced by a much smaller concentration of the particular compound in its cell-fluid than is the case with

the other cells. In some cases, however, this does not appear to be the explanation; for example, the action of barium and potassium salts on the cardiac muscles, and such cases require further research. L. M. J.

Chemistry of Vegetable Physiology and Agriculture.

The Coloration of the Sap of Beetroot and the Soluble Oxidising Ferments. By GABRIEL BERTRAND (*Bied. Centr.*, 1897, **26**, 60—62; from *Bull. Assoc. Chim.*, **14**, 19, and *Neue Zeit. Rübenzuck.-Ind.*, 1896, 253).—The coloration of beetroot sap when exposed to air is due to the action of a soluble ferment belonging to the new group of oxydases. These ferments are readily detected by means of an alcoholic solution of guaiacum resin, a drop of which applied to vegetable sap containing the ferment produces a blue coloration.

The reddening, and subsequent blackening, of beetroot sap, is due to the oxidation of tyrosine, by the combined action of air and an oxydase (tyrosinase). Laccase (another oxydase) has no effect on tyrosine. Whilst tyrosinase is destroyed by heating for 12 minutes at 60—70°, laccase is not entirely destroyed after 20 hours' heating.

Tyrosinase was also isolated from the tubers of dahlia and from *Russula nigrans*. N. H. J. M.

Action of Ammonium Nitrate on Aspergillus niger. By CHARLES TANRET (*J. Pharm.*, 1897, [vi], **5**, 5—8).—When *Aspergillus niger* is cultivated on the surface of a liquid containing 0·25 gram of ammonium nitrate per 100 c.c., the mycelium develops rapidly, and bears spores in less than 24 hours. If two or three times the quantity of ammonium nitrate is taken, the mycelium is formed as before, and reaches enormous proportions; no reproductive organs are, however, produced. In the latter case, the liquid is found to contain free nitric acid, whilst the body of the mycelium contains starch. M. W. T.

Action of Carbonic Anhydride on the Protoplasm of Living Plant Cells. By G. LOPRIORE (*Bied. Centr.*, 1897, **26**, 102—104; from *Jahrb. wiss. Bot.*, 1895, **28**, 531—626; and *Bot. Centr.*, 1896, **66**, 15).—Pure carbonic anhydride has no permanently injurious effect on the streaming movement of protoplasma, but only momentarily hinders it. When 20 or 10 ten per cent. of oxygen is mixed with the gas, the movement of the protoplasma gradually accommodates itself to the large amount of carbonic anhydride, and is then no longer checked in the almost pure gas.

Pure oxygen sometimes accelerates the streaming, but not to the extent often supposed. Pure hydrogen often quickens the movement at first, but afterwards retards it.

Mucor spores cannot germinate in pure carbonic anhydride, but are however, not destroyed by being kept 3 months in the gas. Germination is considerably retarded, but not injured by pure carbonic

anhydride mixed with 70—90 per cent. of oxygen. With less oxygen, the growth of the mycelium is arrested, and there is no formation of sporangium.

The increase of yeast is checked in pure carbonic anhydride, but proceeds when the gas is replaced by air. *Mycoderma cerevisiæ*, however, lost the power of increasing when kept for 12 hours in the pure gas.

Pollen grains vary in their behaviour towards carbonic anhydride according to the kind of plant; some form blistered protuberances which burst after a short time, whilst others do not germinate, or at once burst. Pollen tubes generally burst in pure or diluted carbonic anhydride, and even 1—10 per cent. of the gas considerably hinders growth. N. H. J. M.

The Amount of Iodine in certain Algæ. By ESCHLE (*Zeit. physiol. Chem.*, 1897, **23**, 30—37).—In both *Fucus vesiculosus* and *Laminaria digitata*, the iodine is almost exclusively in the form of an organic compound. The nature of the substance is uncertain, but, from a study of its solubilities, it appears to be a mixture of several substances. W. D. H.

Relation between Lime and the Carbohydrates in Plants. By P. GROOM (*Bied. Centr.*, 1897, **26**, 136—137; from *Naturw. Rundschau.*, 1896, 931).—The accumulation of carbohydrates in plants when calcium is deficient is attributed to the presence of acid oxalate, which prevents the conversion of starch into sugar. Direct experiments showed that hydrogen potassium oxalate retards the action of diastase on starch. The effect of hydrogen potassium oxalate on living plants was first to promote the accumulation of starch, owing to its non-conversion into sugar, and then to retard starch formation, and probably also assimilation of carbon. The final effect of the accumulation of the oxalate was the death of the protoplasm.

N. H. J. M.

Solubility of the Red Colouring Matter of Grapes: Sterilisation of the Musts of Fruits. By AUGUSTE ROSENSTIEHL (*Compt. rend.*, 1897, **124**, 566—569).—The red colouring matter of the grape, contrary to the general belief, is soluble in grape juice when the latter is heated, even in absence of alcohol. The solution takes place more rapidly the higher the temperature, and requires about 5 hours at 70°. The same phenomenon is observed with other fruits containing a red colouring matter.

These colouring matters are very unstable, and are decolorised by contact with tin, bronze, and brass, but are only slightly affected by copper. Exposure to air at 50° renders them quite insoluble, even in alcohol, and it follows that exclusion of air is indispensable if the red colouring matter of the grape and other fruits is to remain in solution. The musts of the grape, and of other fruits, when preserved from contact with air, retain the agreeable taste of the fresh fruit. In absence of air, they can be heated for a long time and repeatedly at 45—50° without undergoing the change known as "goût de cuit." Moreover, repeated heating even at this low temperature results in sterilisation of the musts, which can afterwards be

kept for weeks in the ordinary vessels used for storing wine without undergoing any alteration and without any loss of the colour, odour, or taste of the fresh fruit. C. H. B.

Nutritive Value of Beetroot Leaves. By FRANZ LEHMANN (*Bied. Centr.*, 1897, **26**, 96—99; from *Hannov. Land. u. Forstwirtsch Zeit.*, 1896, No. 44).—Feeding experiments were made with four sheep to ascertain the value of sour beetroot leaves. The following average amounts of constituents digested in (1) unwashed and (2) washed leaves are given, and compared with (3) mangolds:

	Organic matter.	Proteids.	Fat.	Carbohydrates.
1. Beetroot leaves	11·12	0·17	0·34	9·69
2. Beetroot leaves	10·12	—	0·25	9·17
3. Mangolds	9·83	0·15	0·05	8·32

The nutritive value of the leaves, therefore, resembles that of mangolds.

In the process of washing, the leaves lost the following percentage amounts of each constituent: organic matter, 9·0; crude proteid, 36·9; fat, 26·5; crude fibre and nitrogen-free extract, 5·4. The loss of nitrogenous matter is very high, but as the sour leaves contain little digestible proteid (consisting chiefly of undigestible proteids and amides) there is not much actual loss. N. H. J. M.

Preservation and Composition of Hops. By JOHANNES BEHRENS (*Bied. Centr.*, 1897, **26**, 54—57; from *Wochenschr. f. Bierbrauerei*, 1896).—Among the organisms isolated by the author from hops were a bacillus (*B. lupuliperda*) which produces a green fluorescence in suitable solutions, and forms trimethylamine from certain constituents of hops (compare this vol., ii, 115), a kind of *Aspergillus*, and various yeasts. The spontaneous heating of hops is due to micro-organisms, but not always to the same kind. The mould fungi destroy the acids of the hops and produce carbonates from the organic salts.

The following analysis of hops is given. The numbers show the percentage amounts in dry substance free from sand:

Nitrogen								
Total.	Proteid.	Soluble in water.	Ether extract.	Light petroleum extract.	Aqueous extract.	Tannin.	Ash.	HNO_3.
3·26	2·24	1·58	17·15	15·49	24·83	3·59	7·66	trace.

The fresh hops contained water (8·12) and sand (1·65 per cent.).

The coloration of hops (brown or red) is due to insufficient acidity and may be produced by adding alkali. The amount of acid in hops varies with the kind, season, &c.; it raises the acidity of the wort and so essentially influences the process of fermentation. The presence of acid is practically without effect in the sterilisation of the wort. The sulphurisation of hops is effective in improving the colour of hops; it has no effect on their hygroscopic properties. As regards the disinfecting power of sulphurous acid, it was found that whilst an extract of hops which had not been sulphurised soon produced a luxuriant mould vegetation, a similar extract of hops which had been so treated contained only very few and quite sterile mycelium flakes. The effect of sulphurous acid was, therefore, not sterilisation in the ordinary sense,

but to render the hops more or less incapable of becoming infected, a far more important result. N. H. J. M.

Ordinary and Dried Superphosphate. By LOUIS DECOUX and LOUIS DRUMEL (*Bied. Centr.*, 1897, **26**, 79—80; from *L'ingénieur agric.*, 1896, 110).—The results of field experiments in which barley was manured with sodium nitrate alone and in conjunction with ordinary and dried superphosphate respectively, indicated that the ordinary superphosphate was more effective than the dried. The addition of sodium nitrate was advantageous. N. H. J. M.

Effect of Potash Manuring on the Quality of Brewing Barley. By THEODOR REMY (*Bied. Centr.*, 1897, **26**, 15—17; from *Wochenschr. f. Braueri*, 1896, No. 41).—The following conclusions are given with reserve, owing to the limited number of samples available for examination. There is no indication of a favourable effect due to large applications of potash, and potash manuring can only be insisted on when the potash in the soil is insufficient for good crops, and then only with the view of increasing production. On the other hand, the unfavourable effect of a heavy application of potash (in increasing the percentage of nitrogen) is so slight that it need hardly be considered. Too much hope should not be placed in potash as a specific means of producing better barley for brewing. N. H. J. M.

The Rôle of Fat in Manures. By J. HANS VOGEL (*Bied. Centr.*, 1897, **26**, 128—129; from *Deut. landw. Presse.*, 1896, No. 74).—Stable manure, green manure, guano, and crude bone meal contain 0·5—2 per cent. of fat, whilst manure prepared from human excrement contains from 8—9 per cent. Fat would be injurious when, for instance, it is important for the nitrogenous matter to become quickly available to the plant. This, however, does not occur, as in such cases manures free from fat would be applied. Fat would be useful in delaying the decomposition of nitrogenous matter applied in the autumn. In the case of human excrement, the fat slowly decomposes during the autumn but this ceases in winter; in the spring, the fat gradually decomposes, liberating at the same time the nitrogenous matter just at the time it is required for the crop. Loss of nitrogen is thus prevented. The presence of fat is particularly favourable in the case of light, sandy soils. N. H. J. M.

Action of Potassium Salts on different kinds of Soil (*Bied. Centr.*, 1897, **26**, 9—14; from *Arbeiten d. deut. Landw. Ges.*, Heft. 20). —I. *Action of Potassium Salts on Sandy Soil* (MAX MAERCKER).—A number of pot experiments were made with a light sandy soil mixed with 2·5 per cent. of peat, together with different potash manures. The results of the first series of experiments made with lucerne, without potash, with kainite, carnallite and "Hartsalz" (containing 15 per cent. of potash) showed a great increase of produce under the influence of potash. The effect of the three salts was about equal. Potassium carbonate was, however, more effective than any of the three. Sodium carbonate, used in small quantity, gave a slight increase of produce, whilst a larger quantity diminished the yield. The same potassium salts gave similar results with white mustard; sodium

carbonate and chloride, even in small quantities, were injurious. With potatoes, the potash manures had relatively little effect, and the percentage of starch was not materially increased. In an experiment with grasses and *Leguminosæ* (mixed), it was found that where large amounts of potash were given, the produce contained so much potash that the residue in the soil was about the same as when less was applied, and it is concluded that meadows should receive potash every year. The relation of grasses to leguminous plants increased under the influence of potash manure.

II. *Action of Potassium Salts on Peaty Soil* (BRUNO TACKE).—Five series of pot experiments are described. The peaty soil received burnt lime (15 grams), basic slag (containing $P_2O_5 = 2$ and 3 grams), and sodium nitrate (0·8 and 1·5 gram of nitrogen in each pot). Kainite, carnallite, potassium sulphate, "Hartsalz," from Solvayhall, near Bernburg, and potassium magnesium carbonate were added in amounts containing 0·375, 0·5, and 0·625 gram of potash (corresponding with about 75, 125, and 175 kilos. per hectare). The plants selected were oats, wheat, barley, and white mustard.

The results of the experiments showed that the peaty oils required potash in order to give satisfactory results. The grain crops generally had feeble stems unless sufficiently supplied with potash; but large amounts of potash did not materially increase the yield as compared with the less amounts.

The effect of potash on the amount of potash in the produce was very variable. In some cases, the percentage of potash in the produce was about the same when potash was applied as when it was not, and sometimes it was even less. The straw was frequently richer in potash, the grain less frequently, when manured with potash. The percentage of phosphoric acid and nitrogen was generally unmistakably diminished in the plants manured with potash. In rye and barley, the starch was considerably increased under the influence of potash.

In some cases, the soil which had received potash became poorer in potash than it was originally, owing to increased root development under the influence of the manure. N. H. J. M.

Analytical Chemistry.

Barium Thiosulphate as Basis for Iodimetry. By M. MUTNIANSKI (*Zeit. anal. Chem.*, 1897, 36, 220—221. See also Plimpton and Chorley, Trans., 1895, p. 314).—The solubility of barium thiosulphate at 17·5° is such that a saturated solution, prepared by shaking an excess of the salt for 15 minutes with water of that temperature, is of exactly N/100 strength. Such a solution deposits none of the salt when kept for several days at 15°. The barium thiosulphate is prepared by mixing hot concentrated solutions of 5 parts of sodium thiosulphate and 4 parts of barium chloride, and washing the precipitate, first with warm, then with cold water, with 95 per cent. alcohol, and finally with ether. Air drying for an hour suffices to render it fit for use. A

convenient starch indicator is prepared by triturating 5 grams of potato starch and 0·01 gram of mercuric iodide with 30 c.c. of cold water, and pouring the mixture into a litre of boiling water. After boiling for 3 minutes, it is allowed to cool. The clarified solution retains its sensitiveness (1 part of iodine in 3,500,000) for years. M. J. S.

Rapid Estimation of Organic Nitrogen. By LÉONARD (*Chem. Centr.*, 1896, i, 573; from *Rev. Chim. anal. appl.*, 1895, 285).—Ten c.c. of milk or urine is introduced into a long-necked 300 c.c. flask, mixed with 1 gram of dried copper sulphate, 1 gram of dried sodium phosphate, and 10 c.c. of strong sulphuric acid, and boiled until it becomes quite clear and green; when cold, the contents are transferred to a 100 c.c. measuring flask, supersaturated with aqueous soda, and the precipitated copper hydroxide redissolved by adding 20 c.c. of an alkaline solution of Rochelle salt. After making up to the mark, an aliquot part of the liquid is removed with a pipette, and the nitrogen in it is estimated either by distilling off the ammonia or by measuring the volume of nitrogen given off on adding an alkaline solution of bromine. L. DE K.

Estimation of Ammonia in Animal Secretions and Tissues. By MARCELLUS NENCKI and J. ZALESKI (*Chem. Centr.*, 1896, 1, 510—511; from *Arch. exp. Pathol. und Pharm.*, **36**, 385—394).—The finely divided matter, or the liquid, is distilled under diminished pressure at a temperature not exceeding 35°, the ammonia being liberated by means of lime-water, or sometimes by milk of lime. The distillate is collected in a specially constructed bulb-tube containing standard sulphuric acid, the excess of which is afterwards titrated with standard soda, using methyl-orange as indicator. L. DE K.

Microchemical Reaction for Nitric Acid. By REINHARD BRAUNS (*Jahrb. f. Min.*, 1897, 1, 73).—Behrens' methods of first reducing the nitrate to nitrite or to ammonia are not direct, and not always applicable. The author suggests the following. A solution of nitrate gives, with barium chloride, sharply developed, regular octahedra of the sparingly soluble barium nitrate. L. J. S.

Estimation of Very Small Quantities of Nitrous Acid. By LUIGI ZAMBELLI (*Chem. Centr.*, 1896, 1, 1283; from *Mon. Sci.*, [iv], **10**, 351).—The reagent is prepared by dissolving 2 grams of sulphanilide and 2 grams of phenol in 25 c.c. of sulphuric acid mixed with 25 c.c. of water; the syrupy liquid thus obtained is at once ready for use. The liquid to be tested is put into a stoppered cylinder, mixed with 2 or 3 c.c. of the reagent, and after 10 or 15 minutes it is rendered alkaline with ammonia. If nitrites be present, a yellow coloration will make its appearance, which may be matched by using a solution of silver nitrite of known strength, and the amount of nitrous acid thus estimated. L. DE K.

Estimation of Phosphorus in Steel and Cast Iron. By GEORGE AUCHY (*J. Amer. Chem. Soc.*, 1896, **18**, 955—970).—The author recommends the following slight modification of Emmerton's reduction process. The yellow precipitate obtained by treating the nitric acid

solution of iron with ammonium molybdate and ammonium nitrate is dissolved in as small a quantity of ammonia as possible and poured back into the 8-oz. Erlenmeyer precipitation flask; 25 c.c. of dilute sulphuric acid (1 : 2) is added and then 5 grams of zinc, the flask being heated gently for 5 minutes or longer until the zinc is nearly dissolved. A little sodium carbonate is now added, and when effervescence has nearly ceased, the flask is corked and allowed to cool; the solution is filtered from the undissolved zinc through a little cotton wool in a Hirsch funnel of the smallest size, using the pump, and the flask is rinsed three times with cold water, the filtrate being titrated without delay by means of potassium permanganate. The author has proved, by a large number of experiments, that the molybdenum compound corresponds with the formula $Mo_{12}O_{19}$, although this at first may have been Mo_2O_3, which gets oxidised by filtering and dilution.

It sometimes happens that a portion of the yellow precipitate again separates on adding the sulphuric acid, but this may be ignored as it gradually becomes reduced and passes into solution. L. DE K.

Citrate-solubility of Phosphoric Acid. By ARMAND D. HERCZFELDER (*Zeit. angw. Chem.*, 1897, 73—77).—When treating basic slags with Wagner's citric acid solution, a portion of the acid is liable to be precipitated as calcium citrate. Being thus deprived of some of its solvent, part of the phosphoric acid may also be precipitated as ferric phosphate, and thus render the results too low.

The liquid should, therefore, not remain too long in contact with the sample, and must be soon filtered off. Any precipitate which may form afterwards must be redissolved by adding hydrochloric acid.

L. DE K.

Citrate-soluble Phosphoric Acid in Basic Slags. By MAX PASSON (*Zeit. angw. Chem.*, 1897, 82—84).—This is an attempt, partly successful, to calculate the amount of citrate-soluble phosphoric acid from the total citrate-soluble matter, the insoluble portion of the basic slags being collected on a weighed filter and weighed. Further experiments will, however, have to be made. L. DE K.

Modification of the Method of Estimating the Soluble Phosphoric Acid in Basic Slag. By GIOVANNI SANI (*Staz. Sper. Agrar.*, 1895, **28**, 275—276).—The substance (5 grams), mixed with water (100 c.c.), is treated with 10 per cent. citric acid, then with ammoninm citrate (official solution, 200 c.c.) and heated on a water bath for an hour, keeping the mixture carefully stirred. It is then diluted to 500 c.c., and the process continued according to the official method. The results of analysis of two samples made by this modification of the official method, and by Wagner's method, are given, showing close agreement. N. H. J. M.

Reinsch's Test for Arsenic and Antimony. By JAMES L. HOWE and PAUL S. MERTINS (*J. Amer. Chem. Soc.*, 1896, **18**, 953—955).—The authors prefer the Reinsch's copper test for arsenic to using the Marsh's apparatus, as it does not require the destruction of organic tissues, and will still show the presence of one-millionth part of dissolved arsenic. When the copper is heated in a glass tube, the arsenic yields the charac-

teristic sublimate of arsenious acid, appearing as brilliant octahedra under the microscope. If it is not a case of arsenical but of antimonial poisoning, the slowly forming deposit on the copper will be of a decidedly violet tint, very distinct from the iron-grey deposit of arsenic; moreover, the sublimate will show no trace of crystallisation under the microscope. L. DE K.

Reaction of Carbonic Oxide. By ACHILLE E. MERMET (*Compt. rend.*, 1897, **124**, 621—624).—Carbonic oxide reduces a dilute solution of potassium permanganate acidified with nitric acid, and the change is more rapid in presence of silver nitrate. Precautions are necessary to prevent reduction by organic matter contained in the air or in water. Solutions are prepared as follows. *Silver nitrate*, 2 to 3 grams, in 1000 c.c. of water. *Potassium permanganate*: 1000 c.c. of water is boiled for some time with a few drops of nitric acid free from hydrochloric acid, and permanganate solution is added until a rose-colour is persistent. After cooling, 1 gram of permanganate is dissolved in the water, and 50 c.c. of pure nitric acid added, the solution being kept out of contact with dust and away from the light. The test solution is prepared, just before use, by mixing 20 c.c. of silver nitrate solution with 1 c.c. of permanganate solution, adding 1 c.c. of pure nitric acid, and diluting to 50 c.c. with water free from organic matter.

Two flasks with glass stoppers are filled with water free from organic matter, and one is emptied in presence of the air to be tested, and the other in presence of pure air; 25 c.c. of the reagent is poured into each flask, and they are allowed to stand side by side, with as little exposure to light as possible, and the time necessary for the decolorisation of the permanganate solution is observed. With air containing from 1 part of carbonic oxide in 500 to 2 parts in 10,000, the time required for decolorisation varies from 1 to 24 hours. Hydrocarbons and sulphur compounds also reduce the permanganate solution.

The author was unable to detect any carbonic oxide in the gases liberated by plants in active growth. He suggests that the carbonic oxide that is undoubtedly sent into the air in somewhat large quantities is oxidised to oxalic acid. C. H. B.

Modified Method for the Qualitative Analysis of a Mixture of Bases. By L. LAFAY (*J. Pharm.*, 1897, [vi], **5**, 224—228).—The author suggests a method for the detection of the metals not precipitated by hydrogen chloride and hydrogen sulphide. The method does not, however, differ greatly from some of those already in use.

M. W. T.

Detection and Estimation of Small Quantities of Magnesia in Lime-stones. By ALEXANDER HERRFELD and A. FÖRSTER (*Chem. Centr.*, 1896, i, 1283; from *Zeit. Ver. Rübenzuck.-Ind.*, 1896, 284—288). —To make a qualitative test, 0·5 gram of the sample is dissolved in 10 c.c. of water with the aid of hydrochloric acid; any iron is oxidised by means of a little nitric acid and then precipitated by boiling with a small excess of calcium carbonate. After filtering, an excess of limewater is added which precipitates any magnesia present.

After decantation and slightly washing the precipitate, it may be

redissolved in hydrochloric acid, freed from lime by means of ammonia and ammonium oxalate, and precipitated with sodium phosphate. It is then, as usual, weighed as pyrophosphate. L. DE K.

Estimation of Lead in Minerals. By GIOVANNI GIORGIS (*Gazzetta*, 1896, **26**, 522—527).—The author finds that the following method of estimating lead in galena gives good results. About 2 grams of the powdered mineral is treated with nitric acid, the latter displaced by heating on the water bath with sulphuric acid, and the precipitate, if desired, freed from sulphuric acid by washing by decantation, although this is unnecessary. The product is treated with soda or potash, the solution acidified with acetic acid, to the whole or an aliquot part of the solution excess of standard potassium dichromate solution is added, and the liquid made up to a known volume; the excess of dichromate is determined in an aliquot part filtered from the lead chromate, by reducing with sulphurous anhydride, precipitating with soda, filtering and dissolving the precipitate in sulphuric acid, the latter solution being made up to standard volume, and the chromium determined by titration with permanganate by the author's method (Abstr., 1893, ii, 554). The excess of potassium dichromate added to the lead solution is thus known, and when subtracted from the total quantity added gives the quantity which reacted with the lead, so that the percentage of the latter in the mineral can be calculated.

W. J. P.

Quantitative Analysis of Refined Copper. By ERNST MURMANN (*Monatsh.*, 1896, **17**, 697—731).—Wegscheider, in his study of the estimation of copper as cuprous sulphide (Abstr., 1894, ii, 31), having stated that even with careful manipulation an error of 0·3 per cent. might occur, the author has reinvestigated this subject, and finds that cuprous sulphide, prepared from pure copper, and repeatedly heated in hydrogen with the addition of a fragment of sulphur, varies less than $\pm 0{\cdot}05$ per cent. from the theoretical yield. The safest method of heating is to use a large burner, adjust the air until the luminosity just disappears, and place the crucible about 5 cm. from the top of the burner, so that it is completely surrounded by the flame. When a minute trace of hydrogen sulphide is introduced into the hydrogen, by passing the gas through dilute hydrogen sulphide solution, it is both safe and necessary to raise the crucible to a bright red heat. Cupric sulphide prepared in the wet way is far from pure. Calcium and silica from the vessels are always present, the former only in negligible quantity, but silica in sufficient amount to render it essential that the weighed cuprous sulphide should be dissolved and the insoluble matters collected. The largest error, however, is caused by the presence of alkalis, especially when an alkali sulphide has been used to extract antimony, &c.; they can only be removed by washing the precipitate with hydrogen sulphide solution after ignition. In spite of these defects, the estimation of copper as sulphide is the most accurate method available. Silver and lead must first be removed by adding a few drops of hydrochloric acid to the nitric acid solution and then evaporating with a small excess of sulphuric acid. The filtered solution is then precipitated by hydrogen sulphide as usual. The amounts of

gold, tin, bismuth, antimony, and arsenic in refined copper are usually so small that they need not be separated, since they fall within the limits of the error in the copper estimation itself. The electrolytic method is less exact, owing to the tendency of the reduced copper to absorb moisture from the air even in the desiccator. For the estimation of iron and nickel, it is better to precipitate the bulk of the copper as thiocyanate than as sulphide, since the sulphide always carries down small quantities of those metals. In estimating the lead, enough hydrogen sulphide should be added to the copper solution to throw down only a few centigrams of sulphide. This precipitate will contain all the lead, together with some antimony and bismuth. The lead in it should be estimated electrolytically. Antimony and arsenic are best estimated by heating 50—100 grams of the metal to bright redness for 2 hours in a current of hydrogen. The volatile metals are completely expelled, and are condensed partly in the tube, partly (together with the sulphur) in a hydrochloric acid bromine solution; lead passes over at the same time, and must be separated by sodium sulphide. If the antimony is weighed as tetroxide, it must afterwards be purified from alkali salts by washing with cold water. Estimation as trisulphide by heating in carbonic anhydride in a Gooch crucible is inexact, since oxygen enters the crucible by diffusion and partially converts the sulphide into oxides. These can, however, be reconverted into sulphide by heating in hydrogen sulphide. The published instructions for the estimation of oxygen in copper require revision. When filings are taken for heating in hydrogen, it is impossible to clean them without incurring superficial oxidation to an extent which may more than double the amount of oxygen. Since filings also are apt to adhere to the glass of the bulb tube during ignition, the weighing of the tube is involved, but as glass cannot be ignited for long without loss of weight, an error is incurred. The copper is best used in the form of rods 4—6 millimetres in diameter and 10—20 mm. long. These are cleansed from grease by benzene or chloroform, and either filed bright or rubbed with dry sand in a bag and wiped, but not dried by heat. They are best heated in a boat placed in a plain tube. The heat must be continued until the weight becomes constant, which may require several hours. The estimation of the cuprous oxide by treatment with silver nitrate yields very fallacious results, the amount of oxygen found being greater than the total ascertained by ignition in hydrogen.

An analysis of Mansfeld copper conducted according to the above principles gave the following results per cent.:

Cu.	Ag.	Pb.	Fe.	Ni.	Co.	Sb. and As.	S.	O.
99·85	0·015	0·0006	0·0057	0·0012	0·0006	0·0002	0·0014	0·06

and metals in the insoluble residue 0·0007, a far greater degree of purity than has been shown by former analyses. M. J. S.

Estimation of Copper. By RUDOLF WEGSCHEIDER (*Monatsh.*, 1897, **18**, 44—47).—Attention is called to some misconceptions displayed by Murmann (preceding abstract) in his allusions to a paper of the author's (Abstr., 1894, ii, 31). C. F. B.

Acetylene as a Quantitative Reagent. By HENRIK G. SÖDERBAUM (*Ber.*, 1897, **30**, 902—904).—As already stated (this vol., i, 309), on passing acetylene into an ammoniacal solution of a cupric salt, the metal is completely precipitated as black copper acetylide; this precipitation is quantitative, and can be used as a method for the estimation of copper.

Since other metallic solutions are not affected by acetylene, this method can also be employed as a means of separating copper from mixtures containing it; an experiment conducted on a solution containing copper and zinc, showed that no trace of the latter was carried down by the acetylide. J. F. T.

Analysis of Copper Salts. By LIVIO SOSTEGNI (*Staz. Sper. Agrar.*, 1895, **28**, 167—180).—The following method is recommended for analysing commercial copper sulphate. The salt (1 gram) is dissolved in water (25 c.c.) in a small Erlenmeyer flask, and the solution treated with 15 c.c. of a solution of Rochelle salt and sodium hydroxide (in the same proportions as used in Fehling's solution); after adding 25 c.c. more water, it is gradually treated with sugar solution, and boiled for 5 minutes. Freshly boiled water (25 c.c.) is added, the liquid allowed to subside a little, and filtered through a filter free from ash; with a good filter, the cuprous oxide can be washed free from alkali in 5 to 10 minutes. The dried oxide is then put into a platinum boat, together with the burnt filter, and reduced in a current of hydrogen. The copper can be readily removed from the platinum boat; although occasionally a little nitric acid has to be used to dissolve the last traces. The method is quick, and gives very good results. Small quantities of iron do not affect the result. If, however, more iron is present, the solution is heated with a slight excess of ammonia, filtered and boiled; the analysis is then continued as described.

Estimation as Cuprous Sulphide.—The copper is precipitated as cupric sulphide in the manner described by Fresenius (*Quant. Anal.*, vol. I), filtered, and quickly dried. The filter with the precipitate is then burnt on a platinum wire, dropped into a porcelain boat, covered with a little finely powdered sulphur, and heated in a current of hydrogen. The method gives very good results, equal to those obtained by the electrolytic method.

The first method may also be employed for estimating sugar in must and wines, &c. The must (5 c.c.), in a 100 c.c. flask, is treated with basic lead acetate solution (4 c.c.) and 20 per cent. sodium carbonate (4 c.c.), diluted to 100 c.c., and a portion filtered through a dry filter. Of the filtrate, 10 c.c. is treated with 25 c.c. of Fehling's solution diluted with four times its bulk of water, boiled for 2 or 3 minutes, and allowed to cool; the supernatant liquid is poured off through a filter, and the precipitate washed with hot water. The analysis is then continued as described. As regards the relation of the amount of copper to sugar, with solutions containing not more than 0·5 per cent. of sugar, 50 milligrams of sugar seems to correspond with about 96·0 of copper (Meissl), whilst with 0·5—1·5 per cent. solutions, the same amount of sugar corresponds with about 93·7 of copper (Herzfeld). N. H. J. M.

Quantitative Analysis with Aid of Hydrazine Sulphate. By ATTILIO PURGOTTI (*Gazzetta*, 1896, **26**, ii, 559—573).—Hydrazine sulphate may be advantageously used in the estimation of copper, chromic acid, and manganese dioxide, inasmuch as it reduces these substances, giving a quantitative yield of nitrogen.

On boiling copper sulphate solution with sodium chloride and hydrazine sulphate, reaction occurs in accordance with the equation $4CuSO_4 + 10NaCl + N_2H_4,H_2SO_4 = 2Cu_2Cl_2 + 5Na_2SO_4 + 6HCl + N_2$; this reaction is applied to the estimation of copper sulphate in the following way. The aqueous solution of the cupric salt containing excess of sodium chloride is boiled to expel air, in a suitable apparatus, and a slight excess of a well-boiled concentrated solution of hydrazine sulphate introduced; the mixture is then boiled until colourless, the nitrogen collected in a eudiometer, and its volume at N. T. P. ascertained in the usual way. 100 c.c. of nitrogen at N. T. P. is equivalent to 1·1313 gram of copper.

Potassium dichromate reacts with hydrazine sulphate in sulphuric acid solution in accordance with the equation $2K_2Cr_2O_7 + 5H_2SO_4 + 3N_2H_4,H_2SO_4 = 2Cr_2(SO_4)_3 + 2K_2SO_4 + 3N_2$; so that 100 c.c. of nitrogen at N. T. P. is equivalent to 0·87577 gram of potassium dichromate, or 0·59576 gram of chromic anhydride; the determination is carried out just as with cupric salts, but no sodium chloride is used and the hydrazine solution is acidified with sulphuric acid.

Manganese dioxide readily reacts with hydrazine sulphate in acid solution in accordance with the equation $2MnO_2 + H_2SO_4 + N_2H_4,H_2SO_4 = 2MnSO_4 + 4H_2O + N_2$, and in neutral solutions a similar reaction occurs, but hydrazine hydrate is formed; 0·77861 gram of manganese dioxide liberates 100 c.c. of gas at N. T. P. The determination may be performed in acid or neutral solutions, either hot or cold, but if ferric oxide is present it reacts with the hydrazine sulphate in hot acid solution, although not in neutral or in cold acid solutions.

The test analyses gave good results. W. J. P.

Separation of Thorium from the other Rare Earths by means of Potassium Trinitride [Azoimide]. By LOUIS MUNROE DENNIS (*J. Amer. Chem. Soc.*, 1896, **18**, 947—952).—The author has proved by a large number of experiments that thorium may be quantitatively separated from cerium, lanthanium, and didymium by boiling the neutralised solution with a solution of potassium azoimide. The thorium is precipitated as hydroxide, a corresponding amount of azoimide escaping.

The reagent is prepared by nearly neutralising a dilute solution of azoimide with aqueous potash. L. DE K.

Estimation of Thoria and its Behaviour with Oxalic Acid and Ammonium Oxalate. By CHARLES GLASER (*Zeit. anal. Chem.*, 1897, **36**, 213—219).—The author admits the correctness of Hintz and Weber's statement (this vol., ii, 162) that a thoria solution, mixed with a large excess of ammonium oxalate, gives no precipitate even on cooling. The presence of ammonium acetate increases the solubility. Excess of hydrochloric acid completely precipitates the thorium from these solutions, seemingly as the salt $ThH_2(C_2O_4)_3 + 2H_2O$. Zirconium

oxalate is soluble in hydrochloric acid. A separation of thorium from the zirconium oxides by ammonium oxalate is complete only when a larger excess of the oxalate than just suffices for dissolving the zirconium oxalate is avoided. Cerium oxalate is somewhat soluble in ammonium acetate, and the use of a large amount of this salt must therefore be avoided when separating thorium and cerium. M. J. S.

Estimation of Manganese in Cast Iron. By FERDINAND ULZER and JULIUS BRÜLL (*Chem. Centr.*, 1896, i, 769; from *Mitt. techn. Gew. Mus. Wien*, 1895, 312).—The liquid, after being freed from iron by means of zinc oxide according to Volhard's directions, is mixed with 20 c.c. of a 5 per cent. solution of hydrogen peroxide. Aqueous soda is added as long as a precipitate forms, and the mixture is boiled. When cold, standard solution of oxalic acid is added, and then dilute nitric acid, the mixture is heated nearly to boiling, and the excess of oxalic acid in the clear solution is titrated with standard permanganate solution.

The best solvent for the iron is a mixture of 10 vols. of nitric with 2 vols. of sulphuric acid and 10 vols. of water; during the evaporation of the solution, 10 c.c. of hydrochloric acid is added. The liquid should contain about 0·1 gram of manganese. L. DE K.

Estimation of Manganese and Chromium in Products of the Iron Industry. By GIOVANNI GIORGIS (*Gazzetta*, 1896, **26**, ii, 528—536).—The author modifies Volhard's process (Abstr., 1880, 141) for determining manganese as follows. The solution of the blast furnace or other product containing iron and manganese is treated with sodium carbonate until a slight precipitate forms, which is then dissolved by nitric acid free from nitrous acid, and the solution diluted to standard volume. A known volume of N/20 potassium permanganate, more than sufficient to oxidise all the manganese present, is boiled for some time in a basin with a large quantity of sodium nitrate and an aliquot part of the manganese and iron solution; after cooling and diluting to a standard volume, an aliquot part of the solution is separated through an asbestos filter and the excess of permanganate titrated with N/20 chromium sulphate solution. From the excess of permanganate thus ascertained, the quantity of manganese in the original solution can be calculated.

This method is not directly available for the estimation of chromium; if chromium but not manganese be present, the former can be determined by substituting for the sodium nitrate added to the boiling permanganate solution, a solution containing 40 grams of potassium carbonate and 0·5 gram of potash per litre; this is added to the permanganate solution which is then boiled with the chromium solution for a short time, after the latter has been neutralised with sodium carbonate. The excess of permanganate used is determined as before.

If the solution contains iron, manganese, and chromium together, it is treated with sodium carbonate, clarified with nitric acid, and boiled for some time with excess of permanganate containing much sodium nitrate; the liquid is then rendered alkaline by adding the above solution of potassium carbonate and potash, and after again boiling is

made up to a standard volume, an aliquot part filtered off through an asbestos filter, and the excess of permanganate used determined as before. The quantity of permanganate requisite to oxidise both chromium and manganese is thus ascertained, and by determining one of these metals by either of the methods described above, the quantity of each present can be found.

The test analyses gave good results. W. J. P.

Estimation of Tungsten in Ferro-Tungstates. By HEINRICH WDOWISZEWSKI (*Chem. Centr.*, 1896, i, 770; from *Przeglad. Techniczny*, 1896, Zeszyt, I).—About 1 gram of the sample is fused with 6 times its weight of a mixture of 2 parts of dry borax and 3 parts of potassium sodium carbonate; the fused mass on being exhausted with boiling water leaves the ferric oxide undissolved. The filtrate is mixed with excess of hydrochloric acid, evaporated to dryness, and the residue treated with dilute hydrochloric acid, which leaves the tungstic and silicic acids undissolved. The tungstic acid is then dissolved in ammonia, and reprecipitated by adding hydrochloric acid.

L. DE K.

Estimation of Antimony as Tetroxide. By HENRI BAUBIGNY (*Compt. rend.*, 1897, **124**, 499—502).—The existing statements as to the stability of antimony tetroxide at high temperatures are conflicting, and the author has made experiments with a view to ascertain whether antimony can be accurately estimated in the form of this oxide. Pure antimonic acid prepared from the pentachloride by the action of water, and dried at 100°, was heated in porcelain dishes, in a glass or porcelain tube, at 357°, 440°, 550—600°, and 800°. At 357°, the weight becomes practically constant after heating for many hours, and the product seems to be antimonic anhydride. At 440°, decomposition begins and continues as the temperature is raised to 800°, but after 2 hours at the latter temperature the weight of the oxide becomes constant, and it has the composition Sb_2O_4. No further change takes place if the oxide is maintained at 800° for several hours, and it follows that the tetroxide is stable at this temperature. It begins to decompose, however, if the temperature is raised to the melting point of silver. C. H. B.

Estimation of Paraffin in the Last Fractions of Brown-Coal Tar and Crude Petroleum. By D. HOLDE (*Zeit. angw. Chem.*, 1897, 116—117).—The author dissolves the sample in the smallest possible amount of ether and precipitates the paraffin by adding the smallest excess of absolute alcohol. The temperature should be as low as -18 or $-21°$. The paraffin is washed on a weighed filter with a mixture of alcohol and ether of the same temperature.

L. DE K.

Detection of the Adulteration of Essential Oils. By ÉMILE GOSSART (*Bull. Soc. Chim.*, 1896, [iii], **15**, 597—609).—When a mixture of liquids is added drop by drop, with certain precautions, to another liquid mixture, containing the same constituents, the former will not merge at once in the latter, but will assume a spheroidal state when the composition of the two liquids is nearly the same (compare

Abstr., 1892, 236). When, however, the composition of the one differs from that of the other by more than a certain amount, the two liquids mix at once and will not exhibit the above phenomenon. Upon this fact, the author has based a method, to which he gives the name of *homeotropy*, for the detection of the adulteration of certain essential oils. In this method, the suspected oil is allowed to drop from a pipette into a specially constructed glass dish containing some of the essential oil of known purity, when, if pure, it will exhibit the spheroidal phenomenon above described. It is found, for example, that this phenomenon is only manifested by mixtures of oil of bitter almonds and alcohol, when these differ in composition by less than 2 per cent. whenever oil of bitter almonds contains more than 3 per cent. of alcohol, a drop of the mixture invariably merges at once in the pure oil when added in the manner described by the author. In the case of mixtures of oil of bitter almonds and nitrobenzene, it is necessary, on account of the high viscocity of the liquid, to dilute with alcohol when applying this method. Estimations of any given adulterant may be made by adding to the genuine essential oil such measured quantities of the adulterant in question as will give rise to the spheroidal phenomenon with the impure liquid. A. C. C.

Detection of the Adulteration of Essential Oils. By EMILE GOSSART (*Bull. Soc. Chim.*, 1897, [iii], **15**, 666—688, 724—741).—An account of the composition and proportion of the commoner essential oils, of the substances with which they are usually adulterated, and of the application of the author's method (preceding abstract) for detecting or estimating the adulteration. M. W. T.

Volumetric Estimation of Ethylic Alcohol and Ethylic Acetate in Admixture. By BASIL B. KURILOFF (*Ber.*, 1897, **30**, 741—743).—Ethylic alcohol and ethylic acetate are quantitatively converted into acetic acid when they are heated at 100° for 4—6 hours with an acid solution of potassium dichromate, and this method can readily be used for their estimation. The oxidation is effected by means of potassium dichromate (1 gram in 100 c.c.) and dilute sulphuric acid, the excess of chromic acid after the reaction has been completed being determined by means of potassium iodide and sodium thiosulphate. The error in the estimation of 0·1—0·15 gram of either substance is less that 0·5 per cent. To analyse a mixture of acetic acid, ethylic acetate, and ethylic alcohol, three processes are necessary. 1. Titration of the acetic acid. 2. Hydrolysis of the ethylic acetate with excess of baryta water and titration of the excess with sulphuric acid. 3. Oxidation of the total ethylic acetate and ethylic alcohol by potassium dichromate. A. H.

Estimation of Glycerol in Wine and the Indirect Estimation of Mannitol in Mannitic Wines. By G. MANCUSO-LIMA and GIUSEPPE SGARLATA (*Staz. Sper. Agrar.*, 1895, **28**, 236—245).—The wine (25 c.c.) is evaporated to a very small volume in a porcelain dish on a water bath, treated with a slight excess of basic lead acetate and excess of ammonia, and quickly filtered; the precipitate is washed two or three times, the funnel being covered with a larger funnel, the tube of which is connected with a flask containing caustic potash (to avoid

possible decomposition of the lead glucosate by carbonic anhydride during the filtration). The filtrate is collected in a beaker, supersaturated with pure, concentrated sulphuric acid, again filtered, boiled, and permanganate run in until the liquid becomes red, the boiling being maintained. The number of c.c. of permanganate added multiplied by 0·01 gives the amount of glycerol in the 25 c.c. of wine.

Indirect Estimation of Glycerol.—Fifty c.c. of wine is evaporated down, treated with a slight excess of basic lead acetate, filtered, washed, and diluted to 500 c.c. Of this, 250 c.c. is treated with sodium carbonate, filtered, made up to a definite volume and the glucose determined with Fehling's solution. The other 250 c.c. of the solution is saturated with sulphuric acid, filtered, washed, and the boiling solution oxidised with normal permanganate solution. The amount of permanganate required to oxidise the glucose, as determined, is calculated and deducted from the amount actually used. The number thus obtained multiplied by 0·01 gives the amount of glycerol in 25 c.c. of wine.

Indirect Estimation of Mannitol.—The glycerol is determined by the direct method first described. Another 50 c.c. of the wine is treated exactly as for the indirect estimation of glycerol. The number of c.c. of permanganate *minus* the amount corresponding with the glucose and glycerol, multiplied by 0·0089 gives the amount of mannitol in 25 c.c. of wine.

N. H. J. M.

Estimation of Pentoses and Pentosans by Means of the Furfuraldehyde Distillation. By MARTIN KRÜGER and BERNHARD TOLLENS (*Chem. Centr.*, 1896, 1, 576—577; from *Zeit. Ver. Rübenzuck.-Ind.*, 1896, 21—25).—From 2 to 5 grams of the fodder is distilled with 100 c.c. of 12 per cent. hydrochloric acid until 30 c.c. has passed over, another 30 c.c. of acid is then added, and the operation repeated until the distillate no longer reddens paper saturated with a solution of aniline acetate. A solution of phloroglucinol in dilute hydrochloric acid is now added to the distillate, and the whole is made up with acid to 400 c.c. and allowed to remain overnight. The precipitate is then collected on a weighed filter, washed, dried at 97°, and weighed. To calculate the amount of furfuraldehyde, the weight of the precipitate is divided by 1·82 if it does not exceed 0·2 gram; by 1·93 if it amounts to 0·5 gram, and by corresponding factors if it comes between the two.

To calculate the furfuraldehyde into the respective pentosans and pentoses, 0·0104 is first deducted and the difference is multiplied by the following factors: 1·68 for xylan, 2·07 for araban, or 1·88 for pentosans in general, 1·91 for xylose, 2·35 for arabinose, or 2·31 for the pentoses in general.

L. DE K.

Electrolytic Estimation of Copper in Sugar Analysis. By G. TARULLI (*Gazzetta*, 1896, **26**, ii, 485—495).—In order to ascertain whether, in the reduction of Fehling's solution by sugars, the copper may be advantageously estimated electrolytically, the author, after titrating the sugar solution with standard Fehling, determines the copper remaining in solution by weighing it as electrolytically deposited metal, and then dissolves the cuprous oxide which has been filtered off in nitric acid, displaces the latter by sulphuric acid, and after electro-

lysing, weighs the copper originally precipitated, as oxide; the comparison of the quantity of copper in the Fehling solution used with the sum of the two quantities of copper thus deposited electrolytically shows that the process is accurate. Copper may be deposited electrolytically from alkaline Fehling solution and weighed as metal with nearly the same accuracy as from acid solutions. The cuprous oxide is best filtered off through Berzelius filter paper, and Missaghi's suggestion that a piece of glass rod should be placed between the filter and funnel to expedite filtration should be adopted; the oxide is prevented from creeping over the edge of the filter by turning the latter in several millimetres below the top. Instead of converting the cuprous oxide into nitrate and then into sulphate, satisfactory results may be obtained by electrolysing the solution of the oxide in a mixture of 3 parts of nitric acid (sp. gr. = 1·18) and 8 parts of sulphuric acid (sp. gr. = 1·07).

The author finds that, taking Cu = 63·34, inverted cane-sugar reduces 9·77 equivalents of cuprous oxide. W. J. P.

Reducing Powers of Various Sugars Determined by the Electrolytic Process. By G. TARULLI and E. MAMELI-CUBEDDU (*Gazzetta*, 1896, **26**, ii, 495—502).—The authors have determined the reducing powers of various sugars by Tarulli's process (see preceding abstract), using normal and one-fourth normal Fehling's solution. The reducing powers obtained by them and by Soxhlet are given in the following table:

	Tarulli and Cubeddu.		Soxhlet.	
	Normal.	Dilute.	Normal.	Dilute.
Dextrose	10·748	10·632	10·52	10·11
Lactose	7·238	8·559	7·4	7·4
Galactose	10·003	10·187	9·8	9·4
Maltose	8·682	8·02	6·9	—

The observation of Soxhlet and Brumme, namely, that the first portions of dextrose added to Fehling's solution are more completely reduced than the later ones, is confirmed, the authors finding that the cupric-reducing power of the glucose gradually diminishes as its addition proceeds. W. J. P.

Estimation of Sugar in Animal Liquids. By E. RIEGLER (*Zeit. anal. Chem.*, 1897, **36**, 280; from *Wiener med. Blätt.*, 1896, 451).—Fehling's solution is reduced by an excess of phenylhydrazine with evolution of nitrogen. The difference between the volume of nitrogen obtained from 5 c.c. of Fehling's solution and the same after partial reduction by the sugar to be estimated is reduced to grams and multiplied by 2·6. M. J. S.

Estimation of Sugar in Urine. By AUGUSTA JASSOY (*Chem. Centr.*, 1896, i, 578—579; from *Apoth. Zeit.*, ii, 34—35).—The urine,

which, if alkaline, should be acidified with tartaric acid, is fermented in a special apparatus with yeast, and the carbonic anhydride produced is found by noticing the volume of air before and after absorption by aqueous potash.

It is difficult to see in what respect this process is preferable to those ordinarily used, as nothing like the theoretical amount of carbonic anhydride has been obtained by the author. L. DE K.

Estimation of the Caramel on the Surface of Coffee Berries Roasted with Sugar. By WILHELM FRESENIUS and LEO GRÜNHUT (*Zeit. anal. Chem.*, 1897, **36**, 225—233).—Four methods have been proposed for this purpose, namely, those of Neubauer, König, Stutzer, and Hilger. Stutzer's is the one favoured by the Conference of Bavarian Technical Chemists, but the authors, after testing the four methods side by side, give the preference to Hilger's. Neubauer's and König's processes depend on the extraction of the berries with hot water, and the results are unquestionably too high. In Stutzer's process, 10 grams of the unground coffee is shaken for 5 minutes with 250 c.c. of cold water, made up to 500 c.c., the extract decanted immediately, filtered, and its solid contents (drying at 100°) and ash ascertained.

Experiments with coffee to which no sugar had been added show that an appreciable portion of the extractive matter consists of normal coffee constituents, and if these are deducted the results are too low. In Hilger's process, 10 grams of whole coffee is digested three times, for half an hour each time, with 100 c.c. of a mixture of equal volumes of water and 90 per cent. alcohol at atmospheric temperature. Each portion of extract is decanted, and the united extracts are made up to 500 c.c., filtered, and residue and ash ascertained as before. If from the numbers thus obtained there is deducted a constant (1·07 of dry residue, or 0·83 of ash-free residue per 100 parts of dry coffee), which is the average of four experiments on genuine coffee roasted until it has undergone a normal loss of 18 per cent., the remainder may be regarded as representing the caramel present, and agrees approximately with the numbers obtained in Stutzer's method without any deduction.

M. J. S.

Estimation of Alcapton (Homogentisic Acid) in Urine. By GEORGES DENIGÈS (*J. Pharm.*, 1897, [vi], **5**, 50—54).—See this vol., ii, 337.

Estimation of Filicic Acid in Officinal Preparations of the Male Fern. By GIROLAMO DACCOMO and L. SCOCCIANTI (*J. Pharm.*, 1897, [vi], **5**, 61—62).—The aqueous solution of filicic acid, or the rhizome of the fern itself, is extricated with ether and the ethereal extract agitated with a solution of copper acetate. The copper filicate is collected, washed with water and alcohol, dried at 100°, and weighed. Pure ether should be used for the extraction, as the presence of a small quantity of alcohol lowers the solubility of the filicic acid considerably. M. W. T.

Qualitative Examination of Butter. By EMIL JAHR (*Chem. Centr.*, 1896, i, 462; from *Milch. Zeit.*, **24**, 766—767).—The melted

fat is shaken in a test-tube with twice its volume of water at 31°, and the tube is then placed in water at 50°. Margarine readily separates whilst butter remains emulsified for some time. In a mixture of margarine and butter, two distinct layers will be visible.

On adding sulphuric acid, then hydrochloric acid, and finally a little permanganate solution, the margarine retains its yellow colour, and readily separates from the aqueous layer, whereas butter is completely bleached, and separates with difficulty; a mixture of the two will remain more or less yellow, and will partly stick to the sides of the test-tube. If brine is used instead of water, the margarine separates as a clear yellow layer covered at the top and bottom with a flocculent, opaque mass. If as little as 10 per cent. of butter is present, the fat separates as a homogeneous, opaque, dirty yellow mass.

L. DE K.

Detection of Margarine in Cheese. By VON RAUMER (*Zeit. angw. Chem.*, 1897, 77—82).—The author has not obtained satisfactory results by extracting the fat with ether and submitting it to the usual tests, as the fat in cheese is always sensibly decomposed.

Better results are obtained by rubbing cheese with water, and adding a solution of copper sulphate, which causes the formation of a dense precipitate containing the fat, whilst the free fatty acids remain in the mother liquor; the precipitate is finally extracted with light petroleum of low boiling point. L. DE K.

Estimation of Tannin in Wine. By AGOSTINO VIGNA (*Staz. Sper. Agrar.*, 1895, **28**, 19—22. Compare Abstr., 1891, 1399).—Instead of zinc acetate, potash alum may be employed for precipitating the tannin. The process is as follows: 8 per cent. alum solution (40 c.c.) is added to the wine (50 c.c.), and the acid exactly neutralised with ammonia. The mixture is shaken, filtered through a plain filter, the precipitate washed with cold water, and finally washed out into the original dish. It is then dissolved in dilute sulphuric acid (1 : 4) and titrated in the cold with permanganate after addition of a known amount of indigo solution.

The method gives results agreeing with those obtained by the ammoniacal zinc acetate method. N. H. J. M.

Detection of "Saccharin" in Beer. By WAUTERS (*Chem. Centr.*, 1896, i, 576; from *Mon. scient.*, [iv], **10**, 146—147).—Beer containing "saccharin" usually has a low density, and also contains but little solid matter. The author rejects as untrustworthy the tests for "saccharin" based on the detection of its sulphur; the reaction with resorcinol and sulphuric acid is utterly condemned. He considers the best test to be the one based on the formation of salicylic acid, when "saccharin" is gently fused with potassium hydroxide. L. DE K.

Urometer for Small Quantities of Urine. By ADOLF JOLLES (*Zeit. anal. Chem.*, 1897, **36**, 221—223).—A miniature hydrometer (103 mm. in length) with a scale ranging from sp. gr. 1·000 to 1·010, but furnished with weights by which readings up to 1·050 can be obtained with the use of 20 c.c. of liquid. M. J. S.

General and Physical Chemistry.

Molecular Dissymmetry and the Rotatory Power of Active Homologous Compounds. By PHILIPPE A. GUYE and L. CHAVANNE (*Bull. Soc. Chim.*, 1896, [iii], **15**, 177—195 and 275—305).—The authors give a detailed account of the preparation of the various optically active compounds which they have examined (compare Abstr., 1895, i, 202 and 317). The study of these compounds, and of a number of others prepared and examined by different observers, leads to the following generalisations.

1. For any substance containing one asymmetric carbon atom, C *a b c d*, in which the heaviest group alone is allowed to vary, the formula for the product of asymmetry indicates that the rotatory power reaches a maximum, and that the values then decrease; if the heaviest group, *a*, is already large as compared with the other three, the rotatory powers may decrease continually from the first term.

2. In the 23 series of homologous compounds examined, 16 show values of $[\alpha]_D$ which reach a maximum, whilst in the case of the remaining 7 the values of $[\alpha]_D$ decrease regularly with rising molecular weight.

3. In a number of instances, the observed maximum of $[\alpha]_D$ does not coincide with the calculated maximum value of P, although the maximum of P is usually very close to that of $[\alpha]_D$.

4. These results only hold when the compounds are strictly homologous. If, for example, in any series of normal compounds the butylic is replaced by the isobutylic radicle, or an atom of chlorine by an atom of bromine, the regularity is destroyed.

5. Isomeric compounds may therefore have very different rotatory powers, and the rotatory power depends, not merely on the masses of the groups, but on their relative positions one to another. H. C.

Measurement of the Capacity of Polarisation. By C. M. GORDON (*Ann. Phys. Chem.*, 1897, [ii], **61**, 1—29).—For small currents, polarisation is a reversible process, and if E is the force which it sets up, c the capacity, j the current, and t the time, the Kohlrausch formula $E = 1/c\int jdt$ holds; if, however, the current is increased beyond a certain value, the capacity does not remain constant, and the formula no longer applies. When mercury electrodes are used, the capacity depends primarily on the number of dissolved mercury ions in the solution. The capacity in the case of platinum electrodes depends both on the quantity of occluded hydrogen or oxygen and on the concentration of the electrolytes. Resistances can be accurately determined with platinised platinum electrodes, but the values obtained are too great when the electrodes are not platinised. H. C.

Determination of the Dielectricity Constants of some Salt Solutions by the Electrometric Method. By FREDERIC J. SMALE (*Ann. Phys. Chem.*, 1897, [ii], **61**, 625—628).—The dielectricity con-

stants of the following salt solutions were determined, and are given in terms of water as unity :

Normal conc.	KCl.	HCl.	$CuSO_4$.	Mannitoboric acid.
0·001	1·013	0·990	—	
0·002	1·018	1·033	1·012	
0·005	1·034	1·064	1·017	
0·008	1·070	1·090	1·050	
0·010	1·113	1·126	1·086	
0·030	1·160			
0·020			1·128	
0·050			1·155	
0·333				1·007
0·666				1·019

It is especially noteworthy that the solutions have greater dielectricity constants than pure water, but no explanation of this fact can yet be given. The dielectricity constants are not proportional to the conductivities. H. C.

Electrical Conductivity of Nitramide. By E. BAUR (*Annalen*, 1897, **296**, 95—100. Compare this vol., ii, 25).—The electrical conductivity of nitramide at 0° is stated by Hantzsch and Kaufmann (*loc. cit.*) to be $\mu_{32} = 1·95$, and $\mu_{63} = 1·69$; a decrease of conductivity accompanying dilution is inconsistent with the dissociation hypothesis, and the author has therefore performed a series of observations with a specimen of nitramide obtained from nitrourethane, and several times recrystallised. The values obtained are in opposition to the result of the above-mentioned investigators, the electrical conductivity increasing with dilution, and when $v = 63·105$, the conductivity, $\mu = 1·126$; the higher value recorded by Hantzsch and Kaufmann is attributed to the presence of nitric acid in the specimen of nitramide employed.

In considering the isomerism of compounds having the formula $N_2O_2H_2$ (this vol., ii, 26), Hantzsch states that nitramide is 500 times more feebly acidic than acetic acid; the conductivity of acetic acid, however, is observed by the author to be only five or six times greater than that of nitramide, so that if acidity is regarded as nearly proportional to this constant, acetic acid is not more than five or six times more strongly acidic than nitramide. It is, however, approximately true that the dissociation constant of acetic acid is 500 times that of nitramide.

The author is of opinion that the corrected conductivity constant of nitramide differs so considerably from that of hyponitrous acid as to indicate structural isomerism, and not stereoisomerism as advocated by Hantzsch (*loc. cit.*). M. O. F.

Electromotive Force and Partition Equilibrium. By ALFRED H. BUCHERER (*Zeit. physikal. Chem.*, 1897, **22**, 590—597).—The author replies to the criticisms of Luther (this vol., ii, 240), and points out that his deductions were purely thermodynamical, inasmuch as they involved no assumption regarding the state of substances in solution, &c., although experimental facts, not involving any hypotheses or

speculation were of course used. The author further adds instances which he holds are not in accord with Nernst's theory, the fundamental fault of which is, in the author's opinion, that it employs fictitious physical constants instead of the actual ones. L. M. J.

Heat of Formation of Formaldehyde. By MARCEL DELÉPINE (*Compt. rend.*, 1897, **124**, 816—819).—The action of ammonia on aqueous solutions of formaldehyde develops +16·6 Cal. for each molecule of ammonia, and it follows that $6CH_2O$ diss. + $4NH_3$ diss. = $C_6H_{12}N_4$ diss. + $6H_2O$ develops + 66·4 Cal. If the heat of formation of hexamethylene from its elements is taken as −21·9 Cal., it follows that $C + H_2 + O = H{\cdot}CHO$ diss. develops + 40·3 Cal. If −21·3 Cal. is taken as the heat of formation of hexamethylene, that of formaldehyde becomes 40·4 Cal. The heat of dissolution was measured by passing hydrogen mixed with formaldehyde vapour into water, and the value obtained is 15 Cal., which is relatively very high. The heat of formation of gaseous formaldehyde must be +25·4 Cal. C. H. B.

Solutions of Trichloracetic Acid. By PAUL RIVALS (*Compt. rend.*, 1896, **123**, 240—242).—The heat of neutralisation of trichloracetic acid with potassium hydroxide, or with ammonia, varies considerably with the dilution. Thus, a solution of trichloracetic acid containing 1 gram-molecule per litre, when neutralised with a dilute ammonia solution, gave 13·85 Cal., and a solution of the acid containing a gram-molecule in 4 litres gave 13·10 Cal. The difference is mainly due to the heat of dilution of trichloracetic acid, which is found to be very appreciable. The author gives an expression for the heat of solution of solid trichloracetic acid, from which it would appear that the heat of solution in 0·4 litre is zero, that it rises to 2·7 Cal. in 8 litres, and falls to —2·53 Cal. in 0·11 litre. H. C.

Calorimetric Investigations. Heat of Combustion of the Amides and Anilides of the First Members of the Series of Dibasic Acids. By FRIEDRICH C. A. STOHMANN and EMIL HAUSSMANN (*J. pr. Chem.*, 1897, [ii], **55**, 263—284. Compare Abstr., 1895, ii, 482).—The heat of combustion of several amic acids, and of their phenylic derivatives, amides, anilides, imides, ammonium salts, and ethereal salts, has been determined. It is found that phenyloxamic (oxanilic) acid and its derivatives yield appreciably higher values than do the isomeric phthalamic acid derivatives; this is connected with the fact that the first acid has a much higher conductivity constant than the second. Unsymmetrical diphenylcarbamide has a slightly larger heat of combustion than the symmetrical compound; as usually happens in such cases, the first is the compound with the lower melting point. The difference between the heats of combustion of succinic acid and its derivatives and those of the corresponding derivatives of malonic acid is less than the normal difference for CH_2 (156·6 Cal.), and still smaller is the difference between malonic and oxalic derivatives; connected with this is the fact that the conductivity constant of oxalic acid is much greater than that of malonic, and that of malonic acid than that of succinic. The heats of combustion of diamides are greater than those of the corresponding amic acids, and these than those of the corresponding dibasic acids, by 74·9 Cal. in the mean. Using this

number, the heat of combustion of carbonic acid can be calculated from that of carbamide giving the value +2·4 Cal.. Further, the heat of the changes: dibasic acid + ammonia (liquid) = amic acid + water; amic acid + ammonia (liquid) = diamide + water is in both cases 10·2 Cal. in the mean. The heats of combustion of dianilides are greater than those of the phenylamic acids, and these than those of the dibasic acids, by 804·9 Cal. in the mean; hence the heat of the changes: dibasic acid + aniline = phenylamic acid + water; phenylamic acid + aniline = dianilide + water is in both cases + 5·8 Cal. in the mean. The formation of a diamide or dianilide (and water) from the ammonium or aniline salt of the acid, and also that of an imide (and water) from an amic acid, is accompanied by a slight absorption of heat, except in the case of the phthalic derivatives, where there is a very slight development of heat. The substitution of phenyl for hydrogen in the amido-group increases the heat of combustion by 730·1 Cal. The heat change: dibasic acid + ammonia (liquid) = diammonium salt is 2 × 13·7 Cal.; that of oxalic acid + aniline = aniline oxalate is 2 × 9·65. The heat of the change: amic acid + alcohol = alkylic amate + water is − 1·5 Cal.; using this number, the heat of combustion of phenylcarbamic (carbanilic) acid can be calculated to be 801·1 Cal., and that of carbamic acid itself to be 70·6 Cal. The actual experimental results are given below, in so far as they appear to be new.

	Heat of combustion.	Heat of formation.
Oxamic acid	132·0	159·5
Phenyloxamic acid	863·1	130·4
Phenylmalonamic acid	1013·4	143·1
Phenylsuccinamic acid	1166·5	153·0
Phthalamic acid	850·7	142·8
Phenylphthalamic acid	1577·9	117·6
Phenylcarbamide	880·0	51·0
Diphenylcarbamide, sym	1612·8	23·2
,, unsym.	1614·2	21·8
Tetraphenylcarbamide	3075·0	−35·0
Oxamide	203·3	122·7
Phenyloxamide	937·5	90·5
Oxanilide	1665·4	64·6
Malonamide	358·8	130·2
Dimethylmalonamide, sym	686·0	129·0
Diethylmalonamide, sym	995·1	145·9
Phenylmalonamide, anhydrous	1088·9	102·1
,, cryst.	1088·7	136·8
Diphenylmalonamide	1818·0	75·0
Succinamide	509·7	142·3
Phenylsuccinamide	1244·6	109·4
Succinanilide	1971·3	84·7
Phthalamide	921·7	106·3
Phenylphthalamide	1651·1	78·9
Diphenylphthalamide	2383·2	48·8
Succinimide	438·1	110·4
Phenylsuccinimide	1168·5	82·0
Phthalimide	850·2	74·3
Phenylphthalimide	1579·1	47·4
Ammonium oxalate	193·8	270·2
,, malonate	349·6	277·4
,, succinate	502·8	287·2
,, phthalate	923·0	243·0
Aniline oxalate	1662·3	205·7
Ethylic carbamate	397·5	126·0
,, phenylcarbamate	1128·3	62·7
Methylic oxamate	304·7	149·8
Ethylic oxamate	457·7	159·8
Ethylic phenyloxamate	1191·2	128·3
Aniline	810·7	−5·2

C. F. B.

Modification of the Beckmann Apparatus. By WILHELM MEYERHOFFER (*Zeit. physikal. Chem.*, 1897, **22**, 619—625).—The author describes a form of Beckmann apparatus available either for freezing point or solubility determinations, both of which give points on the temperature/concentration curve. A diagram of the apparatus is given and experiments are recorded on the freezing point depression of phenol by thymol at various concentrations. The chief features in the apparatus are (1) the use of a Witt stirrer, with the thermometer in its hollow axis, and (2) a form of "inoculating pencil" whereby, by

the introduction of a minute portion of solidified mass, overcooling is avoided. L. M. J.

Measurement of Freezing Point Depressions. By E. H. Loomis. (*J. Physical Chem.*, 1897, **1**, 221—231).—The author compares the method of determining the freezing points of dilute solutions employed by Abegg (Abstr., 1896, ii, 587) with his own (Abstr., 1894, i, 228). In both cases, the convergence temperature is made to practically coincide with the freezing point of the solution by employing a cooling bath, the temperature of which is only very slightly below the freezing point, by protecting the solution from radiation from without, and, finally, by working in a room at a low temperature. The error due to the change of concentration of the solution owing to the separation of ice is reduced to negligible dimensions in both cases by supercooling the solutions to a very small extent. Although these objects are attained in different ways, the two methods are in principle identical.

A comparison of the results obtained shows them to be almost identical with few exceptions; the differences are less than the differences of two sets of observations made by Abegg.

The author concludes, from the experimental data, that the errors in Abegg's determinations are still of the order of 0·02°, but that the principle of the method is free from objection, and consequently the accidental variations could be eliminated by making several series of observations on each substance. At present, notwithstanding the advances made in the experimental methods, few, if any, trustworthy results have been obtained with solutions more dilute than 1/100 normal. T. E.

Freezing Point depressions of Magnesium Chloride. By Jacobus H. van't Hoff and H. M. Dawson (*Zeit. physikal. Chem.*, 1897, **22**, 598—608).—The authors determined the melting point depression of hydrated magnesium chloride, $MgCl_2 + 6H_2O$, by various compounds, using for the purpose the apparatus described by Meyerhoffer (preceding page). The salt itself melts at 116·67° with the formation of liquid $MgCl_2 + 6{\cdot}18\ H_2O$ and precipitation of solid $MgCl_2 + 4H_2O$. By means of carbamide and of glycerol, the value 76 was obtained for the normal molecular depression. Potassium chloride gave the same value, the maximum depression obtained corresponding with that due to the saturated solution, $MgCl_2$, 0·026 KCl, 6·18 H_2O. Sodium chloride also gave the normal value, the saturated solution being $MgCl_2$, 0·004 NaCl, 6·18 H_2O. Hydrated magnesium sulphate gave a low value, and greater difficulty was found in obtaining a constant depression; this was found to be due to the partial, but, on standing, complete, precipitation of the sulphate as kieserite. Potassium sulphate gave, at first, an abnormal value of about 230, that is, three times the normal depression, which may be due to dissociation into three ions, or more probably to the formation of potassium chloride and magnesium sulphate, with later precipitation of kieserite, so that the final value is, as found, that due to the saturated solution of potassium chloride. Kainite gave a depression equal to the sum of those due to magnesium sulphate and potassium chloride. Magnesium bromide

gave a depression of about one-fourth the normal value, the low value being expected from the isomorphism of bromides and chlorides.

L. M. J.

Influence of Superfusion on the Freezing Points of Aqueous Solutions of Sodium Chloride and Alcohol. By FRANÇOIS M. RAOULT. (*Compt. rend.*, 1897, **124**, 885—889).—The author has previously shown (*Rev. sci.*, 1886, 603) that the relation between the observed and the real reduction of the freezing point in aqueous solutions is given by the expression $C = C'(1—KS)$ in which C is the true reduction, C' the observed reduction, S the superfusion, and K a coefficient which remains constant for the same apparatus and mode of operating. He also showed that the error due to superfusion could be reduced to 0·01°, a quantity negligible in practice though not in theoretical investigations. It follows that, for the same degree of superfusion, the same apparatus, and the same mode of operating, the ratio C/C' is constant, and it would seem that the error due to superfusion is without influence on the significance of the results (this vol., ii, 11). This view has been widely adopted, but it is not in agreement with the facts.

The author has determined the freezing points of aqueous solutions of sodium chloride and alcohol with the apparatus previously described (*Compt. rend.*, **122**; this vol., ii, 89) and with the precautions already indicated, especially with regard to coincidence between the converging temperatures and the freezing point. Experiments were made with superfusions of about 0·5°, 1·0° and 1·5°, the results being plotted with the superfusions as abscissæ and the observed reduction of freezing points as ordinates. The point at which the curve cuts the axis of the ordinates gives the reduction of freezing point when the superfusion is nil. From the data thus obtained, the value of K in the above expression for a given degree of superfusion can be ascertained: $K = C'—C/C'S$.

The results are given in tabular form. Contrary to the general belief, the value of K is not independent of the concentration, and may become twice as great, as the degree of dilution increases. When $S = 1°$, the value of K may be as much as 2·5 per cent. of the observed reduction, and the ordinary correction in which the value of K is taken as 0·0125 is insufficient, especially in very dilute solutions, the effect of the error being to alter the curve of molecular reductions and raise its point of origin. The true molecular reductions for $S = 0°$ vary in a very different manner in the two cases of sodium chloride and alcohol. With the former, they increase rapidly when the dilution becomes very great, and tend to a maximum value of 37·4, corresponding with ionisation (*loc. cit.*); in the case of the latter, the value of the molecular reduction, 18·3, is independent of the degree of dilution, as Arrhenius predicted.

C. H. B.

Determination of Molecular Weights. V. By ERNST BECKMANN (*Zeit. physikal. Chem.*, 1897, **22**, 609—618).—[With C. SCHULTEN]. —When, during freezing, a solid solution separates in place of the pure solvent, the resulting molecular weight is always too high, and in this case the true value may be obtained by the use of a

third compound, which does not form a solid solution, as in the author's experiments on the molecular weight of iodine (Abstr., 1895, ii, 382). Experiments were therefore performed with acetic acid, benzoic acid, and α-benzaldoxime for which abnormal molecular weights are also obtained by other methods and are regarded as due to association. Benzene was employed as the solvent and bromoform as the third compound, and in each case the ratios of the quantities of acetic acid, &c., and bromoform in the crystal mass and liquid were equal, so that no solid solution is formed, and the abnormal values for the molecular weights are due to complexes. In the case of thiophen, the results were quite different, the ratio of thiophen to bromoform being much less in the liquid than in the solid, the values for ratio (in solution) ÷ (ratio in crystals) varying from 0·379 to 0·449, so that thiophen and benzene form a solid solution. When this is allowed for in the calculations, the molecular weight of thiophen is obtained as 78·1 in place of 133·3, which is found if no correction is made.

[With H. PFEIFFER].—The molecular weight of selenium as obtained by vapour density determinations decreases from $Se_{2·8}$ at 860 to $Se_{2·08}$ at 1420 ; it therefore seemed probable that, at ordinary temperatures, a high value would be obtained, and determination of the freezing point of solutions of selenium in phosphorus gave values corresponding with $Se_{7·6}$, a result closely analogous to those obtained with sulphur (Abstr., 1890, 447 ; 1891, 260).

The author further describes a modification of the form of apparatus previously described (this vol., ii, 88), whereby the electro-magnetic stirrer is avoided by the use of a mechanical stirrer working through an air-proof mercury joint, and a practically similar method due to Kaiser is also appended. L. M. J.

Exact Cryometry. By A. PONSOT (*Compt. rend.*, 1896, **123**, 557—559).—A reply to Raoult's criticism of the author's results (this vol., ii, 88).

Application of the Clapeyron Formula to the Melting Point of Benzene. By R. DEMERLIAC (*Compt. rend.*, 1896, **122**, 1117—1118). —The change in the melting point of benzene, with a change in pressure of one atmosphere, is calculated by the Clapeyron formula and found to be 0·02936°. The value found experimentally between the limits 1 and 10 atmospheres is 0·0294°. Between these limits of pressure, the formula therefore holds, but it does not apply outside these limits. H. C.

Verification of the van der Waals Law of Corresponding Conditions. By ÉMILE H. AMAGAT (*Compt. rend.*, 1896, **123**, 30—35). —In all attempts that have hitherto been made to test the van der Waals law of corresponding conditions, one great source of error and objection has been found in the uncertainty of the determined values for the critical data. In order to avoid this difficulty in the comparison of substances with one another, the author constructs the isothermals of a number of compounds to arbitrary scales of pressure, and reduces the resulting diagrams by photographic process to corresponding scales of pressure. The superposed curves should then show coincidence, and the result is quite independent of the absolutely

determined values of the critical pressure or critical volume. A complete coincidence is, in fact, found for carbonic anhydride, air and ether, and an almost as complete agreement for carbonic anhydride and ethylene. The law of van der Waals is, therefore, in these cases fully confirmed. H. C.

Van der Waals' Law of Corresponding Conditions and the Determination of Critical Constants. By ÉMILE H. AMAGAT (*Compt. rend.*, 1896, **123**, 83—86).—The coincidence in the isothermal curves of different substances constructed to corresponding scales of pressure, which has been demonstrated by the author (preceding abstract), renders possible a determination of critical data by comparison of the curves obtained; for the critical points must coincide, and it will therefore be only necessary to read off the co-ordinates of the one system (B) which correspond with the critical co-ordinates of any standard system (A). Thus, taking the critical constants of carbonic anhydride as the standard, those of ethylene, ether, and air are found to be as follows:

	Carbonic anhydride.	Ethylene.	Ether.	Air.
Critical temperature	31·35°	8·8°	195°	−140·7°
„ pressure (in atm.)	72·9	48·5	36·5	35·9
„ volume	0·464	0·212	0·253	0·344

H. C.

Liquefaction of Mixtures of Two Gases. By PIERRE DUHEM (*J. Physical Chem.*, 1897, 1, 273—297).—The phenomenon considered in this memoir was first observed by Cailletet (*Compt. rend.*, 1880, **90**, 210). A mixture of 1 volume of air and 5 volumes of carbonic anhydride liquefies partially under a moderate pressure, whilst, on increasing the pressure, it again evaporates. The two pressures approach each other as the temperature rises. Analogous observations were afterwards made by van der Waals and by Andrews. The author, in 1888, pointed out that the phenomena might be accounted for by supposing that, for certain concentrations of the gaseous mixture, the dew curve (the curve representing the pressures under which a given gaseous mixture will just deposit liquid at given temperatures) is of such a form that at certain temperatures there are two points on the curve which correspond with the same temperature. Kuenen (*Arch. Néerl*, 1892, **26**, 394), whose measurements were made with the object of testing van der Waals' molecular theory of a fluid consisting of two different compounds, showed that the dew curve really has this form. The pressure first increases with rising temperature up to a certain point, T say, after which it increases with falling temperature, the curve terminating at a point, θ, called the point of folding. Above T, no condensation can take place; between T and θ, normal condensation followed by retrograde condensation can occur, whilst below θ only normal condensation is possible. At the point of folding, θ, the liquid and gaseous mixtures become identical, and at this point the dew curve of the gaseous mixture meets the boiling curve of the liquid mixture of the same composition. Kuenen supposes that these two curves meet so as to form a single line, and that it is always the dew

curve which is cut twice by a straight line at right angles to the temperature axis. This leads to the conclusion that the phenomenon of retrograde condensation must be capable of being observed with every gaseous mixture of the two substances, whereas if the dew curve and the boiling line meet to form a cusp, this is not necessarily the case. By means of considerations of a mathematical nature, which cannot be reproduced in brief, the author concludes that the former view is the correct one, and shows that all the observed phenomena may be deduced from it. T. E.

Simplified Formula for Calculating the Changes in Density of Liquids with the Temperature. By PHILIPPE A. GUYE and CHARLES JORDAN (*Bull. Soc. Chim.*, 1896, [iii], **15**, 306—308).—Thorpe and Rücker (Trans., 1884, 135) give a relationship between the specific volumes V and V', and the densities D' and D at the temperatures T' and T in the case of any liquid, which may be expressed by

$$\frac{V}{V'} = \frac{D'}{D} = \frac{aT_c - T'}{aT_c - T}.$$

Here V and D are the specific volume and density corresponding with the absolute temperature T, V' and D' are the volume and density corresponding with the absolute temperature T', T_c is the critical temperature on the absolute scale, and a is a constant for all substances, of the value 1·995. Since T_c is connected with the boiling point on the absolute scale T_e by the formula $T_c/T_e = 1{\cdot}55$, substituting in the above $T_e \times 1{\cdot}55$ for T_c, we get

$$\frac{V}{V'} = \frac{D'}{D} = \frac{3{\cdot}09T_e - T'}{3{\cdot}09T_e - T}.$$

This holds for liquids the molecules of which contain from 4 to 25 atoms, but with a greater number of atoms in the molecule the constant has a smaller value than 3·09. The authors therefore conclude that for every substance the constant has an independent value a', which could be found for any one substance by making two determinations of V at different temperatures, when $a' = (TV - T'V')/T_e(V - V')$. It is shown that for ethylic butylic succinate, the value $a' = 2{\cdot}6056$ gives calculated values which are in agreement with the observed for temperatures ranging from 20° to 200°. H. C.

Partition Coefficients and Abnormal Diffusion. By GUSTAV TAMMANN (*Zeit. physikal. Chem.*, 1897, **22**, 483—491).—If a substance is in equilibrium in two different phases, the concentration is in general different in the two, but as the system, either by alteration of pressure or of temperature, approaches its critical state, the partition coefficient approaches the limiting value of unity. This may be illustrated by a solution of triphenylrosaniline in a mixture of benzene and acetic acid (slightly aqueous) at temperatures varying from 0° to the critical temperature 18°, and is deduced theoretically from consideration of the internal pressure of the solutions. The unequal partition of a substance also explains cases of abnormal diffusion, that is, motion of dissolved substance from places of lower to places of higher osmotic pressure. Examples of such cases are given where the liquids employed are methylic or ethylic alcohol and water, and the dissolved

substance, a dye, is originally equally concentrated in both solvents. Alkali-blue diffuses to places of higher osmotic pressure, that is, from the alcoholic to the aqueous layers; sodium triphenylrosanilinetrisulphonate is peculiar, inasmuch as a maximum value for the partition coefficient is obtained for a certain alcoholic-water mixture; methylene-blue behaves in a manner the reverse of that of alkali-blue, diffusing to the more alcoholic layers; nigrosine, indigocarmine and malachite-green behave similarly to alkali-blue. Iodine was found to diffuse from ether or amylic alcohol to acetone, and experiments with sugar solutions and water showed that dyes diffuse to the layers poorer in sugar. By the use of two dyes, such as methylene-blue and nigrosine, two opposite diffusion streams can be set up. Similar differences are observed with different membranes, thus a pig's bladder dissolves far more methylic alcohol than ether, but the reverse obtains with caoutchouc, so that the diffusion streams in mixtures separated by these membranes can vary with the membrane employed. L. M. J.

Equilibrium between Amalgams and Electrolytes. By A. OGG (*Zeit. physikal. Chem.*, 1897, **22**, 536—538).—Mercury and an aqueous solution of silver nitrate react until a final equilibrium is reached between the amalgam formed and the solution of silver and mercurous nitrates, whilst, similarly, between a silver amalgam and mercurous nitrate the reverse action occurs. In this case, if the mercury be present in excess, its active mass may be regarded as constant, whilst that of the silver is proportional to its concentration in the amalgam, and hence, as the salts are also approximately equally dissociated at equal concentrations, the equilibrium constant is given by the equation $a = k\ b\ c$ where a and b are the concentrations of the silver and mercury salts in the solution, and c that of the silver in the amalgam. This relation was tested by a series of 10 experiments at 82°, in which the concentration of the silver varied from 0·004 to 0·05, the values for k being in close accord. The heat of formation of the amalgam was calculated by the use of Nernst's expression,

$$q = 4{\cdot}56 \log k_2/k_1, T_1T_2/(T_2 - T_1),$$

the values obtained from experiments at 15°, 53°, and 90° varying from 2500 to 3400 cals. L. M. J

Chemical Equilibrium, &c., of Metallic Mixtures. By WALTHER NERNST (*Zeit. physikal. Chem.*, 1897, **22**, 539—542).—In the case of the equilibrium of a homogeneous metallic mixture with an electrolytic solution, the necessary condition is $RT/n_1{\cdot}logP_1/p_1 = RT/n_2{\cdot}\log P_2/p_2$ where P_1 and P_2 are the solution tensions of the metals, p_1 and p_2 the osmotic pressures of their metallic ions in the solutions, and n_1 and n_2 the equivalency of the metals. This reduces to $(P_1/p_1)^{\frac{1}{n_1}} = (P_2/p_2)^{\frac{1}{n}}{}_2$, a result shown by Ogg (preceding abstract) to hold in the case of silver and mercury, where $n_1 = n_2$. The potential difference between the alloy and the liquid is given by either of the values $RT/n{\cdot}\log P/p$, and the quantities of metals dissolved or precipitated by a current may differ, the ratio of the amounts for an infinitely small current being in the case of equivalent metals equal to the ratio of their ion concentrations. L. M. J.

Influence of Water on the Solubility of Hydrated Compounds in Alcohol and Ether. By Eyvind Bödtker (*Zeit. physikal. Chem.*, 1897, 22, 505—514).—In order to study the lowering effect of water on the solubility of salts in alcohol, the author determined the ratio of the concentrations of water and anhydrous salts in the case of alcoholic solutions of cupric chloride and cobalt chloride. These concentrations (grams per 5 c.c.) being represented by C_w and C_s, it was found in solutions of the copper salt that the value $C_wC_s^2$ does not yield a constant, so that dissociation $CuCl_2 2H_2O \rightleftarrows CuCl_2 + 2H_2O$ does not take place. The product C_wC_s is approximately constant for small values of C_w, but at higher concentrations $C_sC_w^{\frac{1}{2}}$ gives a more satisfactory value, so that the results indicate a dissociation represented by $CuCl_2,2H_2O \rightleftarrows CuCl_2,H_2O + H_2O$, with the formation of double water molecules at higher concentrations. Cobalt chloride gave analogous results indicating a dissociation, $CoCl_2,6H_2O \rightleftarrows CoCl_2,5H_2O + H_2O$, with association of water molecules. Hydrated calcium chloride is also more soluble in concentrated than in slightly aqueous alcohol, but with the other salts examined the solubility is too small for accurate measurement. The behaviour of oxalic acid in aqueous ether gave anomalous results, which indicate a greater solubility of water in ether containing oxalic acid than in pure ether, this being, in the author's opinion, due to the existence in the ethereal solution of a compound of oxalic acid and water. L. M. J.

New Method Proposed by Etard for the Curve Representation of the Solubility of Salts. By E. Lenoble (*Bull. Soc. Chim.*, 1896, [iii], 15, 54—58).—According to Etard, if the solubility y of a salt is expressed by the percentage of salt in the solution at any temperature x, then $y = a + bx$, where a and b are constants, and the solubility curve is a straight line. In this case, if y is transformed from the Etard notation to that of Gay-Lussac, and the solubility Y calculated in terms of the amount of salt dissolved by 100 parts of the solvent, $Y = 100(a + bx)/(100 - bx - a)$, and the solubility curve in this case should be hyperbolic. The author tests this conclusion in the case of potassium chlorate, but finds that it does not hold, the solubility curve being at least one of the fourth degree. Etard's method of representation does not give a straight line, but a more complex curve. H. C.

Relation between the Velocity of Inversion and the Concentration of the Hydrogen Ions. By Wilhelm Palmaer (*Zeit. physikal. Chem.*, 1897, 22, 492—504).—Previous experiments have shown that the velocity of inversion of sugar by acids is not strictly proportional to the concentration of the hydrogen ions, but decreases more rapidly when the dilution is great, and the author has, therefore, investigated the cause of this at concentrations varying from N/10 to N/1000. Three important sources of error were found to affect the results: (1) neutralisation of the acid by the alkali of the glass; (2) impurity in the sugar; (3) the birotation of the glucose. The impurity found in commercial sugar was largely chalk, and hence, even if present to a very small extent, its importance increases with dilution, so that it is necessary to use sugar as pure as possible, and

yielding the minimum of ash; that employed by the author left a residue of 0·002 per cent. The effect of alkali in the glass was avoided by the use of platinum vessels, and the birotation was allowed for in the calculations. When these precautions were taken, (the required velocity) ÷ (concentration ratio) was found to be practically constant, giving a decrease of about 10 per cent. from N/10 (in glass vessels) to N/100 (platinum), and afterwards remaining constant within experimental errors, the limits for five experiments being 1863 and 1844. L. M. J.

Inorganic Chemistry.

Formation of Hydrogen from Iron and Water. By W. LETTERMANN (*Chem. Centr.*, 1896, i, 952—953; from *Diss. Giessen*).—In investigating the action of steam on hot iron, a porcelain tube containing the iron shavings, and packed at the ends with broken porcelain to ensure a uniform temperature of the gases, was employed. Instead of steam, nitrogen saturated with steam was used, as this method admits of the ready calculation of the weight of water sent over, and the tension of the steam, and also of easy regulation of the velocity of the stream. The nitrogen was sent from a gas-holder, at constant pressure, through flasks containing alkaline pyrogallol, and then into a Varrentrapp's bulb apparatus completely immersed in a water bath; the bulb was weighed before and after the experiment. Before entering the tube, the mixed gases were superheated by passing through a steel tube heated to below 300°. The temperatures were determined by means of the bulb-shaped platinum pyrometer of P. Freyer and V. Meyer (Abstr., 1892, 680). After traversing the tube, the gases pass through a U-tube immersed in water, in which most of the excess of water collected, then through a calcium chloride tube, and finally into a gas-holder with constant mercury level. Other conditions remaining the same, the formation of hydrogen was found to decrease with increase of the speed of the nitrogen stream, particularly at lower temperatures. More hydrogen is evolved at higher temperatures than at lower, the action beginning at 300°, and giving the best yield at 800°. E. W. W.

Commercial Production of Tellurium. By J. FARBAKY (*Zeit. angw. Chem.*, 1897, 11—18).—A method is described whereby tellurium is produced on the large scale from gold tellurium ores. The ore is slowly thrown into boiling concentrated sulphuric acid, when lead, copper, zinc, tellurium, and also a portion of the silver compounds present go into solution, gold and silicic acid remaining undissolved. The product is then heated with water containing from 10 to 15 per cent. of hydrochloric acid, when the latter precipitates the dissolved silver and dissolves the hydrated tellurium oxide precipitated by the water. On filtering, a residue of gold and silver is obtained which is worked up separately. Sulphurous anhydride is passed through the filtrate, and as this takes place in sulphuric or hydrochloric acid solu-

tion, only tellurium and selenium are thrown down. This residue is found to contain from 72—85 per cent. of tellurium, and after a repetition of the process, the percentage is increased to 97—98. The crude powder is melted and cast in moulds. A. W. C.

Oxidation of Nitrogen by means of Electric Sparks or the Electric Arc. By FRANZ VON LEPEL (*Ber.*, 1897, **30**, 1027—1030. Compare Lord Rayleigh, Trans., 1897, 181).—The best yield of nitric acid is obtained under the following conditions. The electrodes are placed in the lower expanded extremity of a perpendicular glass tube of 2—3 litres capacity. The lower cathode is in the form of a flat plate, whilst the upper anode is pointed. A moderately rapid stream of air is kept passing through the apparatus, and a fine liquid spray is forced in from above, this dissolves the nitric acid as it is formed, and the acid solution can be drawn off below. A solution containing 0·56 per cent. of nitric acid was obtained with a cylindrical vessel of 1·75 litres capacity, whilst with a spherical vessel of 1 litre capacity the amount of acid was only 0·31 per cent.

The yield of acid increases more rapidly with an increase in the strength of the current than with an increase in the length of the sparks; if the air is not kept in motion, the nitric peroxide is destroyed almost as quickly as formed.

The amount of air present, the nature of the electrodes, and also the nature of the liquid spray, greatly affect the yield of acid. Liquids which can act as oxygen carriers, for example, magnesium sulphate or calcium permanganate, increase the yield of acid (compare L. Meyer, Abstr., 1888, 216); ozonised air and Röntgen rays, however, appear to decrease the yield. J. J. S.

Hyponitrous Acid. By EDWARD DIVERS (*Annalen*, 1897, **295**, 366—370. Compare this vol., i, 67, and ii, 25).—The author claims priority in the discovery of the hyponitrites, which Hantzsch and Kaufmann attribute to Maumené (*loc. cit.*). M. O. F.

Constitution of Nitramide. By JOHANNES THIELE (*Annalen*, 1897, **296**, 100—110).—The formula, $NH_2\cdot NO_2$, adopted by Thiele and Lachmann in representing nitramide (Abstr., 1896, i, 208), has been opposed by Hantzsch, who has endeavoured to establish a stereoisomeric relationship between this substance and hyponitrous acid, $HO\cdot N\dot{:}N\cdot OH$ (this vol., ii, 26). The present paper is devoted to criticism of Hantzsch's view, support of the original formula being derived from the difference in electrical conductivity of nitramide and hyponitrous acid (Baur, this vol., ii, 358) and also from the production of dimethylnitramine, $NMe_2\cdot NO_2$, when diazomethane acts on nitramide, it having been shown that this agent exhibits a marked tendency to yield oxygen methyl ethers (compare Degner and von Pechmann, this vol., i, 264). M. O. F.

Nitramide. By ARTHUR R. HANTZSCH (*Annalen*, 1897, **296**, 111—119. Compare foregoing abstract).—A reply to the criticisms of Thiele and Baur on the author's view of the constitution of nitramide. M. O. F.

Hypophosphorus Oxide. By J. ADOLPHE BESSON (*Compt. rend.*, 1897, **124**, 763—765).—Hydrogen phosphide has no action on phosphorus oxychloride at its boiling point, but in presence of a small quantity of hydrogen bromide interaction takes place at about 50°, and continues until the hydrogen bromide is all volatilised as phosphonium bromide. Hydrogen chloride is liberated and a reddish-yellow solid is formed. The same product is obtained by the action of hydrogen phosphide on the bromine derivatives of phosphorus oxychloride and also by the action of phosphonium bromide on phosphorus oxychloride in sealed tubes at 50°. Since the two substances do not interact at the ordinary temperature, the phosphonium bromide is conveniently obtained by passing dry hydrogen phosphide into a solution of carefully dried hydrogen bromide in phosphorus oxychloride.

The red product retains chlorine tenaciously and is best purified by heating it with phosphorus oxychloride in sealed tubes at 100° for several hours, repeatedly extracting with boiling carbon bisulphide, and then washing with boiling water, and afterwards drying in a vacuum at first over sulphuric acid at the ordinary temperature and afterwards at 100°. It then has the composition P_2O and is a reddish-yellow, very light, pulverulent solid, stable in presence of air up to 100°, but taking fire when heated more strongly. When heated at about 135° in a vacuum, it slowly loses oxygen. Nitric acid acts on it in much the same way as on phosphorus, and chlorine also acts on it with incandescence at the ordinary temperature. In presence of carbon tetrachloride, chlorine converts it into phosphorus tri- or pentachloride, without any formation of oxychloride; bromine, on the contrary, converts it into a mixture of the oxybromide with the tri- and penta-bromides, whilst iodine converts it into the di-iodide PI_2 without any formation of oxyiodide. The oxide yields no acid when heated with water or a solution of an alkali, and hence it cannot be regarded as a true hypophosphorous anhydride but it stands to hypophosphorous acid and the hypophosphites in the same relation as nitrous oxide to hyponitrous acid and the hyponitrites.

In addition to hypophosphorous oxide, the action of phosphonium bromide on phosphorus oxychloride yields pyrophosphoryl chloride $P_2O_3Cl_4$ and metaphosphoryl chloride, PO_2Cl.

Phosphonium iodide acts on phosphorus oxychloride below 100° with liberation of hydrogen chloride and formation of the iodide P_2I_4, red phosphorus, which obstinately retains iodine, and metaphosphoryl chloride. C. H. B.

Diamonds in Steel. By LEON FRANCK [and, in part, ETTINGER] (*Chem. Centr.*, 1896, ii, 573; from *Stahl u. Eisen*, **16**, 585—588).—Various kinds of steel were treated, as Moissan describes, with nitric, hydrofluoric, sulphuric acids, &c. From unhammered steel, an iron-carbide, FeC_4, a carbide crystallising in octahedra, and probably of the composition Fe_3C_2, and a number of modifications of carbon were obtained. Amongst the last, minute, well-formed octahedra, which sank in methylenic iodide and on combustion left little ash, were observed. From rolled steel, fragments of diamonds with distinct diamond structure were obtained in small quantity. Examination of fifty

varieties of steel led only in few cases to negative results. Higher magnifying powers revealed more numerous diamonds. The very small diamonds only visible under powers of from 2500 to 3000 were apparently attacked by strong oxidising agents. E. W. W.

Compounds of Ammonia and of Methylamine with Halogen Salts of Lithium. By J. BONNEFOI (*Compt. rend.*, 1897, **124**, 771—773).—At $-18°$, dry lithium chloride rapidly absorbs ammonia, and forms the compound $LiCl,4NH_3$, the dissociation curve of which has been determined between $-12°$ and $+18°$. Its dissociation pressure is 760 mm. at 13·3°. At 18°, the compound $LiCl,3NH_3$ is formed, and its dissociation pressure is 760 mm. at 57·5°. At 63°, the compound formed is $LiCl,2NH_3$, and at 85° $LiCl,NH_3$. In dilute solutions, ammonia has no action on lithium chloride, and the ammoniacal lithium chlorides are completely dissociated by water in the proportion of 2 litres to 1 gram-molecule of lithium. The heat of dissolution of the compound $LiCl,3NH_3$ at 15° is $+0·37$ Cal., and since that of lithium chloride is $+8·43$ Cal., it follows that $LiCl + 3NH_3$ gas develops $+34·46$ Cal. $(11·48 \times 3)$. The corresponding values for the compound $LiCl,2NH_3$ are $+2·67$ Cal. and $+23·36$ Cal. $(11·68 \times 2)$ respectively. The conversion of $LiCl,2NH_3$ into $LiCl,3NH_3$ develops therefore $+11·10$ Cal.

Comparing these values with Isamberts results (Abstr., 1878, 697), it follows that the heat of combination with ammonia is lower the more dissociable the compound. Clapeyron's formula gives $+11·09$ Cal. for the mean heat of combination with NH_3, and this agrees well with the experimental results.

Lithium chloride also absorbs methylamine, and at 0° forms the compound $LiCl,4NH_2Me$, the dissociation pressure of which is 760 mm. at $+30°$.

Dry lithium bromide forms the compound $LiBr,4NH_3$ at $-18°$, and its dissociation pressure is 760 mm. at 63°. C. H. B.

Silver Diphosphide. By A. GRANGER (*Compt. rend.*, 1897, **124**, 896—898).—When phosphorus vapour is passed over finely-divided silver heated at 400°, combination takes place, and if the tube is cooled suddenly whilst still full of phosphorus vapour, a product of definite composition, *silver diphosphide*, AgP_2, is obtained. It is soluble in nitric acid, and is attacked by chlorine, bromine, and aqua regia. When heated in a current of inert gas at the temperature of its formation, the diphosphide is completely decomposed. No combination of silver with phosphorus takes place, and hence the metal, like gold, has the peculiarity of combining with phosphorus at 400°, giving it up at 500°, and again retaining it at 900°.

Silver is not attacked by phosphorus trichloride at any temperature below that at which the silver phosphide is decomposed, and the products are silver chloride and phosphorus. The phosphide can, however, be obtained by the action of phosphorus on silver chloride at 300—400°.

The so-called silver sesquiphosphide of Schrötter was probably identical with this diphosphide. C. H. B.

Magnesium Phosphates. By HEINRICH STRUVE (*Zeit. anal. Chem.*, 1897, **36**, 289—298).—The author has prepared three new compounds of phosphoric acid and magnesia. The first, which has the formula $2MgO,P_2O_5 + 7H_2O$ is obtained by dissolving ignited magnesia in boiling orthophosphoric acid until the acid reaction has nearly disappeared. It separates from the boiling solution as a heavy, white, crystalline powder, which under the microscope is seen to consist of rhombs and six-sided plates, showing double refraction. The air-dried substance loses no water at 100°. On ignition, it becomes anhydrous without change of form. A salt of the same composition has been prepared by Hager by mixing highly concentrated solutions of sodium phosphate and magnesium sulphate, and exposing the gelatinous magma to a low temperature (8°), when it contracts to a crystalline sediment.

The second salt, $2MgO,P_2O_5 + 15H_2O$, is prepared by adding to a dilute solution of sodium phosphate sufficient magnesium sulphate to redissolve the precipitate formed at first; it separates gradually in large, colourless, striated, prismatic crystals. At 100°, these crystals lose $9H_2O$, and the whole on ignition. The third salt, which when air-dried has the same composition, is obtained by precipitating a moderately dilute solution of magnesium sulphate with one of sodium phosphate, and passing carbonic anhydride through the magma until complete solution takes place. After discontinuing the passage of the gas, the salt separates in small, colourless, prismatic crystals. It differs from the second salt in losing only $8H_2O$ at 100°, or more slowly at atmospheric temperature. When preserved in a stoppered bottle, it decomposes into the first salt and water. The solubility of the three salts is 1 part in 4000 of water. All three acquire a brownish-yellow colour, and strongly marked striation when dehydrated. The striation is undoubtedly due to the formation of tubular cavities, as is shown by the way in which the dehydrated crystals absorb neutral dyes, such as magenta.

M. J. S.

Solubility of Mercuric Chloride. By DOUGLAS MCINTOSH (*J. Physical Chem.*, 1897, 1, 298—300).—Étard (Abstr., 1892, 558) found that the curve of solubility of mercuric chloride consists of two branches which intersect, the temperature at which the intersection occurs depending on the solvent used. This should not be the case if the change in the slope of the curve is due to a change of one modification of solid mercuric chloride into another. The author finds that when methylic alcohol is used as solvent, $HgCl_2$ crystallises out at temperatures above 40°, $HgCl_2,CH_3\cdot OH$ separating below 35°. The intersection of the two branches of the curve occurs at 38·8°. The addition of water to the alcohol depresses the transition temperature. The author considers it probable that mercuric chloride forms compounds similar to the above with other organic solvents.

T. E.

Effect of a High Temperature on Copper, Bismuth, Silver, Tin, Nickel, and Cobalt Sulphides. By A. MOURLOT (*Compt. rend.*, 1897, **124**, 768—771).—When heated in the electric furnace, cupric sulphide is converted into cuprous sulphide, and the latter fuses and is reduced to metallic copper. Cupric sulphate is also reduced to the metal under the same conditions. Bismuth sulphide is readily

reduced. Silver sulphide melts and is readily reduced; but reduction is not quite complete, and the condensed drops of the volatilised metal retain traces of sulphur. Stannous sulphide, when not very strongly heated, becomes crystalline, but at a higher temperature volatilises. The condensed product has, however, still the composition of stannous sulphide, which, therefore, is a remarkably stable compound. Nickel sulphide is first converted into a non-crystalline, bronze-yellow sub-sulphide, Ni_2S; and this, when more strongly heated, loses all its sulphur, the reduced metal combining with about 6 per cent. of carbon, about 5·5 per cent. existing as graphite. Cobalt sulphide is readily obtained by heating the anhydrous sulphate in a small electric furnace; at a higher temperature, it loses all the sulphur, and the metal combines with about 4·7 per cent. of carbon, 4·5 per cent. being in the form of graphite. C. H. B.

Fergusonite Metals; Philippium. By M. MARC DELAFONTAINE (*Chem. News*, 1897, **75**, 229—230).—To extract philippium, the ore is treated in quantities of 500 grams in a leaden vessel with 1500 grams of strong hydrofluoric acid, the products are repeatedly treated with water, and the insoluble fluorides decomposed in a platinum dish with sulphuric acid; sodium dioxide is then added to oxidise any uranous salts in the solution, the earths are precipitated by oxalic acid, and the ignited precipitate treated with nitric acid. Philippium may be separated from the mixed nitrates by fractional decomposition by heat, or by fractional precipitation with dilute ammonia or with potassium hydrogen oxalate, the separation depending in all cases on the lower basic energy of philippium. The author prefers the fractional decomposition by heat: the mixture of nitrates is heated until quiet fusion has ensued for some minutes, and when cool the red, vitreous mass is treated with water, the treatment of the soluble portion being repeated until no coloured residue is left. If all the residue dissolves, the solution is digested with dilute ammonia in a warm place for some hours, and subsequently decomposed at a higher temperature. The sub-salts obtained in this way are subjected to new series of decompositions until a bright, orange-yellow, basic nitrate is obtained, which dissolves slowly in moderately dilute nitric acid to a deep orange-red, transparent solution. Philippium forms philippous and philippic salts corresponding with a white and an orange oxide. The first salts are colourless, stable, and crystallise well, and do not seem to give any absorption spectrum in solution. Of the *potassium philippous* salts:—the *sulphate* is soluble in a saturated solution of potassium sulphate; the *formate* crystallises very slowly from a syrupy solution in fibro-radiated masses; the *oxalate*, dried at 130°, yields on ignition 51·5 per cent. of orange-coloured oxide; the *nitrate* is colourless and crystalline, but, on fusion, yields a reddish glass, partially soluble in water, and apt to form a solution difficult to filter. *Philippic oxide* is deep orange-red, the moist *hydroxide* being light yellow; with cold, moderately dilute nitric acid, it gives a yellow solution, with the strong acid it effervesces, becomes hot, and yields colourless philippous nitrate; with hydrochloric acid, chlorine is evolved, and it gives proto-salts; it is dissolved by other acids when boiled in the presence of alcohol.

Philippium is more closely allied to cerium and terbium than to any other of the cerium metals; but the behaviour of the salts set forth above distinguishes it even from these metals. D. A. L.

Aluminium Amalgam. By DMITRI P. KONOWALOFF (*Chem. Centr.*, 1896, ii, 338; from *Pharm. Zeit. Russ.*, **35**, 328—329).—The use of aluminium amalgam as a reducing agent has been recommended by Hans Wislicenus and Kaufmann, as in many cases it produces insoluble products, hence no new substances are introduced into solution. The author has investigated the action of water on this amalgam. The amalgam prepared as described by the authors mentioned above, after washing with alcohol, ether and light petroleum, was dried in a current of dry air. It does not act on alcohol containing only a little water, even on boiling, but by gradually increasing the amount of water until it reaches about 11·36 per cent. a solution is obtained which is attacked by the amalgam on boiling, with liberation of hydrogen. Acetic acid containing only 0·1 per cent. of water is attacked by the amalgam with evolution of more hydrogen than corresponds with the water present, but after the action there is no perceptible alteration in the freezing temperature of the acid; with larger quantities of water, however, the freezing point becomes higher, owing to the production of basic aluminium acetate which withdraws a portion of the water.

E. W. W.

Formation of Manganese Compounds. By ODIN T. CHRISTENSEN (*Chem. Centr.*, 1896, ii, 151; from *Oversigt Videnskabernes Selskabs Forhandlinger*, 1896, 94).—The author did not succeed in preparing a manganese alum. Manganic salts are conveniently prepared by a method which depends on the oxidation of manganous salts by permanganic acid: $Mn_2O_7 + 8MnO = 5Mn_2O_3$. Thus manganic phosphate is obtained by warming a saturated solution of orthophosphoric acid, to which a little acetic acid is added, with manganese sulphate and a saturated solution of potassium permanganate. Manganous salts easily become oxidised in alkaline solution, and reduce Fehling's solution with separation of cuprous oxide and formation of manganic tartrate. This solution can be used repeatedly as an oxidising agent, since after reduction it reabsorbs oxygen from the air. Ignited manganese sesquioxide is attacked by organic acids such as lactic and pyrotartaric acids with rise of temperature, and in the case of the former an odour of acetaldehyde becomes apparent, and a manganous salt is formed.

E. W. W.

Preparation of Pure Iron. By HICKS and O'SHEA (*Chem. Centr.*, 1896, i, 293; from *Electrician*, 1895, 843).—Pure iron is obtained by electrolysing a 5 per cent. solution of ferrous chloride to which ammonium chloride has been added in quantity sufficient to form the double compound $FeCl_2,2NH_4Cl$. Any ferric chloride which on electrolysis would form ferric hydroxide, is removed by shaking with pure iron in powder. During electrolysis, the content of iron must not be allowed to become less than 20 to 30 per cent. of the original quantity, and the cathode should be kept completely immersed in the solution. The thin copper plate which serves as cathode is cleaned by

washing with dilute nitric acid, rubbing with cotton wool and fine sand, washing with potassium cyanide solution and finally with water. Swedish iron plate, containing 0·027 per cent. of sulphur and 0·049 per cent. of carbon, is used for the anode, and is placed in a porous cell in order to prevent the spongy carbon separated at the anode from reaching the cathode. The sulphur goes into solution as sulphate, and must be removed from time to time with the anode liquor. A current of 0·08 to 0·2 ampère per 100 sq. cm. of cathode surface at about 0·7 volt. is employed. The iron is obtained as a compact, silver white precipitate of velvety appearance. E. W. W.

Production of Iron Carbide by Direct Combination of Iron and Carbon. By HENRI MOISSAN (*Compt. rend.*, 1897, **124**, 716—722).—The researches of several previous observers have shown that fused or annealed steel contains a crystalline carbide of the composition Fe_3C, and the author has extended these observations to cast iron and the products of the direct action of carbon on iron.

Blooms from three different high blast furnaces were examined in the usual way, but no traces of diamonds could be discovered.

Pure iron was heated with sugar-charcoal in the electric furnace; the mass became more and more viscous as the temperature increased, but regained its limpidity as it cooled, and the cold metal was found to contain only about 1 per cent. of carbon in combination. It would seem, therefore, that carbon and iron combine at a high temperature, but the compound dissociates as the temperature falls. Nickel behaves similarly. It had been observed in the preparation of the diamond that the interior of the metal contained brilliant crystals similar to iron boride or iron silicide. It seemed that the conditions necessary to ensure combination are to avoid complete saturation of the iron by carbon and the formation of graphite; Swedish iron, therefore, was heated in a carbon crucible for 3 minutes with an arc from a current of 900 ampères and 600 volts., and the fused mass cooled quickly by pouring it into water. The product was a very hard and brittle metal, often very highly crystalline, and containing very little graphite, but from 3 to 4 per cent. of combined carbon. In order to isolate any carbide that might be present, the author employed (*a*) the electrolytic method of Mylius, Foerster and Schoene (this vol., ii, 39), and (*b*) the action of very dilute acids out of contact with air. With small quantities of carbide, a stronger acid may be used. Normal nitric acid yields the carbide mixed with a little carbon, whilst the half-normal acid yields the practically pure carbide. In order to remove the small quantity of carbon and liquid hydrocarbons that may be mixed with the carbide, the latter is treated with nitric acid as free from water as possible, and is afterwards poured into a large quantity of water, washed with alcohol and ether, dried at 100° in a current of carbonic anhydride, and allowed to cool in the gas. Instead of the treatment with nitric acid, the impure carbide may be boiled with a 10 per cent. solution of chromic acid.

The iron carbide thus obtained forms brilliant white crystals of the composition Fe_3C; sp. gr. = 7·07 at 16°. It seems to be identical with the carbide present in steel (*loc. cit.*), and is not acted on by oxygen

at the ordinary temperature, although it is somewhat rapidly decomposed by moist air containing carbonic anhydride. When heated, it ignites more easily the finer its state of subdivision, and when very finely divided ignition takes place in air below 150°. It becomes incandescent in sulphur vapour at about 500°, in chlorine below 100°, in bromine vapour at about 100°, and is decomposed by iodine, at a red heat, without incandescence. Hydrogen chloride decomposes it at about 600° with liberation of hydrogen containing a small quantity of hydrocarbons. Concentrated nitric acid has no action on even the finely divided carbide, but on adding a small quantity of water decomposition takes place readily. Dilute acids attack the carbide less rapidly than they attack metallic iron. When heated with dilute hydrochloric acid in sealed tubes, the carbide is decomposed with liberation of a mixture of hydrogen and methane, the proportion of the latter being higher the more concentrated the acid. Water and concentrated solutions of sodium chloride or magnesium chloride have no action on the carbide at 150°. C. H. B.

Metastannyl Chloride. By RODOLPHE C. ENGEL (*Compt. rend.*, 1897, **124**, 765—768).—When sticks of tin, about 5 mm. in diameter, are immersed in nitric acid of sp. gr. 1·3 or 1·4, a reaction takes place without any notable rise of temperature, and the product when washed with water and dried in the air has the composition $(SnO_2)_n(H_2O)_{2n}$; 400 grams of this product is mixed with 100 c.c. of hydrochloric acid of 22° B., and after about 15 minutes solution is complete; the gummy-looking mass is then diluted with water and filtered. If now the filtered liquid is mixed with an equal volume of hydrochloric acid, a finely-divided, amorphous, white precipitate is formed, but settles very slowly. The supernatant liquid contains some stannic chloride, and it follows that the metastannic acid prepared in the manner described is mixed with some stannic acid. The precipitate, when washed with hydrochloric acid of 22° B. diluted with its own volume of water, and dried first on unglazed porcelain, and afterwards in a vacuum over sulphuric acid and potassium hydroxide, agglomerates to translucent, deliquescent masses, which dissolve in small quantities of water or absolute alcohol. The concentrated aqueous solution can be diluted with water if a small quantity of hydrochloric acid is added previously. An excess of hydrochloric acid produces a precipitate; the addition of water without acid also gradually produces a gelatinous precipitate, which, after being washed and dried, will recombine with hydrochloric acid to reproduce the original compound. The soluble chloride has the composition $Sn_5O_9Cl_2,4H_2O$, and the gelatinous precipitate produced by water is the metastannic acid of Fremy, $Sn_5O_{11}H_2,4H_2O$.

It follows that the chloride obtained in the manner described is metastannyl chloride. Stannic chloride in aqueous solution is gradually converted into the metastannyl chloride, which differs completely from the ordinary oxychlorides, such as are formed by dissolving stannic acid in a solution of stannic chloride. The oxychlorides, for example, are not precipitated by hydrochloric acid, but are converted into stannic chloride. Dilute sulphuric acid does not precipitate solutions of metastannyl chloride, and it thus differs from the β-chloride.

The author's experiments indicate the existence of a second metastannyl chloride corresponding with a second metastannic acid, and this will be described in a subsequent paper. C. H. B.

Crystalline Thorium Nitrate. By OTTO FUHSE (*Zeit. angw. Chem.*, 1897, 4, 115—116).—When a solution of thorium nitrate is evaporated and allowed to crystallise in a warm place, large, well-formed crystals belonging to the quadratic system are obtained. They contain $6H_2O$. A. W. C.

Separation of Thoria from Zirconia. By M. MARC DELAFONTAINE (*Chem. News*, 1897, 75, 230).—The powdered ore or oxides is fused in a platinum crucible with twice its weight of potassium hydrogen fluoride; the zirconia is extracted from the solidified mass in the form of K_2ZrF_6, by means of boiling water containing a few drops of hydrofluoric acid; the insoluble fluorides, on treatment with sulphuric acid and ignition below a dull, red heat, yield sulphates of thorium, cerium, and other earths; these are dissolved in water, precipitated by oxalic acid, and the oxalates treated with saturated hot ammonium oxalate, which dissolves the thorium salt. D. A. L.

Bismuth Dichloride. By VICTOR THOMAS (*Bull. Soc. Chim.*, 1897, [iii], 15, 758—760).—When bismuth dichloride is heated in air or in nitric oxide, the products are identical with those which would be formed from a mixture of bismuth with the trichloride. This is in agreement with Schneider and Weber's statement, that on heating the dichloride alone, it breaks up into the trichloride and the metal.
M. W. T.

Action of Air and Nitric Peroxide on Bismuth Iodide and Bromide. By VICTOR THOMAS (*Bull. Soc. Chim.*, 1897, [iii], 15, 760—762).—The author has already shown that bismuth trichloride in presence of nitric peroxide in the cold, produces a nitro-chloride, which, when heated, decomposes, forming the oxychloride BiOCl.

With the tribromide and triiodide in the cold, the oxybromide and trioxide are formed respectively. In the presence of air, the trihaloïds form the corresponding oxy-compounds. M. W. T.

Physiological Chemistry.

Hammerschlag's Method of Estimating the Specific Gravity of Blood and Serum. By LEO ZUNTZ (*Pfluger's Archiv*, 1897, 66, 530—543).—Hammerschlag's method consists in placing a drop of blood in a mixture of benzene and chloroform, and then adding more of one or the other reagent until the drop neither falls nor rises; then the specific gravity of the mixture is taken. The method gives very inconstant results, because diffusion occurs between the blood and the reagents; they and a large number of other possible reagents which were tried are therefore not indifferent either to blood or serum.

W. D. H.

The Antagonism of Substances in the Blood which accelerate and hinder Coagulation. By KARL SPIRO and ALEXANDER ELLINGER (*Zeit. physiol. Chem.*, 1897, **23**, 121—159).—The circulating blood is believed to contain antagonistic substances which respectively hinder and hasten coagulation. In shed blood, the latter get the upper hand. In 'peptone blood' and 'leech extract blood,' there is an increase of the hindering substances; and immunity to peptone injection is caused when the hastening substances are no longer overbalanced in this way. Nuclein, on the other hand, causes intravascular coagulation by producing a preponderance of the hastening substances. The question of the nature of these substances is hardly touched on, but an analogy is drawn between them and toxins and antitoxins. W. D. H.

Freezing Point of Milk. By J. WINTER (*Compt. rend.*, 1897, **124**, 777—778).—Polemical, in reply to Bordas and Génin.

Non-identity of Lipases of Different Origin. By MAURICE HANRIOT (*Compt. rend.*, 1897, **124**, 778—781).—Solutions of the serum and of the pancreatic juice of the dog were prepared so that both had the same hydrolysing effect on monobutyrin in presence of the same excess of sodium carbonate. When, however, they were exactly neutralised, and left in contact with monobutyrin for 20 minutes, the quantity of acid liberated by the serum solution was nearly twice as much as that liberated by the pancreatic solution. It follows that the sero-lipase acts energetically in an acid medium, whilst the activity of pancreato-lipase is greatly reduced under the same conditions.

If solutions are prepared of equal activities at 15°, the activity of the sero-lipase becomes half as great again at 30° and twice as great at 42°, whereas the activity of pancreato-lipase remains constant through the same interval of temperature. Further, the sero-lipase solution retains its activity for several months, whilst the pancreato-lipase solution rapidly alters, and loses its activity after a few days.

Direct experiments show that the blood of the eel contains the same lipase as the blood of the horse, but in much larger quantity. The activity of lipase from the serum of the horse increases with the alkalinity of the solution, and with 2 grams of sodium carbonate per litre, it may become four times as great as under normal conditions.

Since the ferment of the blood that has the power of rendering proteids soluble has its activity increased by the presence of alkali, it follows that the smallest variations in the alkalinity of the blood, whether due to natural causes or produced by the administration of such medicines as sodium hydrogen carbonate, must exert an appreciable effect on the processes of assimilation. C. H. B.

Estimation of Sugar. By EDUARD PFLÜGER (*Pflüger's Archiv*, 1897, **66**, 635—640).—Argutinsky has found that muscle free from fat and glycogen, and fatigued by work, is richer in nitrogen and slightly so in carbon, but poorer in oxygen. This result has not been published before, methods having to be devised for accurately determining the fat and carbohydrate of muscle; the method now given for the estimation of sugar is a modification of Allihn's. The

main objection to Allihn's method is that asbestos chemically unites with copper, and so some of this metal is lost. The main point about the new method is that the copper is weighed as cuprous oxide after drying on the filter at 120°. W. D. H.

Diphtheria Antitoxin. By T. GREGOR BRODIE (*J. Pathol. and Bacteriol.*, 1897, **4**, 460—464).—These experiments were undertaken with the view of determining the nature of the substance present in the antitoxic diphtheria serum prepared from certain horses, which produces a rash. The results are at present incomplete. It was found that ether, alcohol, acetone, and chloroform extract a substance of an irritating nature from the dried serum; whether this is the material sought for is uncertain. The antitoxic properties of the serum are considerably weakened when redissolved; this is in part due to the process adopted, and the longer the precipitate is left in contact with the precipitant (acetone, or more rapidly with alcohol), the greater is the loss of power due to coagulation of proteid matter. The antitoxin itself is probably proteid in nature; its solubilities are those of a globulin; it will not pass through a gelatin filter, and its power is readily destroyed by dilute alkalis, less readily by dilute acids. W. D. H.

Ethereal Hydrogen Sulphates in the Urine under the Influence of Drugs. By MAX MOSSE (*Zeit. physiol. Chem.*, 1897, **23**, 160).—Dermatol and tannigen have no influence on the excretion of ethereal hydrogen sulphates. Tannalbin increases it; actol diminishes it. In spite of the bactericidal influence of silver chloride in plate cultures, neither it nor argonin lessens the excretion; alcohol also has no effect. W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Carbon Compounds as Food Material for Bacteria. By THEODOR BOKORNY (*Pflüger's Archiv*, 1897, **66**, 114—144).—The experiments described in this paper were mostly made with 0·1—0·2 per cent. solutions of different carbon compounds; and mixtures containing several species of bacteria were employed, but they are not specified. Bacteria will grow in solutions of many strong antiseptics of about this strength. The usual mineral salts were also added in each case; the amount of these did not exceed 0·2 per cent. The experiments were carried on at a temperature of 25—30°, and as a rule required 3—6 days, or even longer, before the bacteria grew rapidly.

Methylic alcohol appears to be a fairly good source from which bacteria can obtain their carbon; ethylic and amylic alcohols can also be used. Propylic alcohol serves as a food for fungi, but not for bacteria, whereas benzylic alcohol in 0·1 per cent. solution is a strong poison. Bacteria grow in a 0·08 per cent. solution of phenol, and fungi in a 0·05 per cent. solution. Orthocresol (0·1 per cent.), quinol (0·05), resorcinol (0·05), catechol and phloroglucinol, pyrogallol (0·05), gallic and

tannic acids, will not serve as food material for bacteria; the two latter, however, allow of the growth of fungi. Ethylene glycol, and glycerol are extremely good, whilst tetramethylethylene glycol,

$$OH\cdot CMe_2\cdot CMe_2\cdot OH,$$

is totally useless as food supply.

Different organic acids have also been experimented with, mostly in neutral solutions. There is one species of bacteria which is capable of assimilating formic acid. Acetic, lactic, succinic, tartaric, propionic, aspartic, glyoxylic, pyruvic, levulinic, salicylic, parahydroxybenzoic, and benzoic acids can all be assimilated by bacteria, although benzoic acid acts as a poison to yeast. Oxalic, valeric, citraconic, and mesaconic acids, amido- and nitro-cinnamic acids, cinnamic, hydrocinnamic, and phthalic acids are of no use as food material. Ethylic acetate, ethylic acetoacetate, methylal (1 per cent.), hexamethylenetetramine, acetone, acetaldehyde (0·07 per cent.) can be assimilated, but not glyoxal (0·5 per cent.), paraldehyde, or benzaldehyde. Most carbohydrates, for example, cane-sugar, fructose, *d*-glucose, galactose, milk-sugar, arabinose, sorbose, inosite, mannose, and xylose are extremely good food materials; rhamnose, however, does not act so well. Among cyano- and amido-compounds, acetamide, leucine, methylamine, asparagine, peptone, creatine, and oxamide are extremely useful as sources from which bacteria can obtain their carbon. Nitraniline, anisidine, propylamine, and carbamide are of but little use; whilst ethylenediamine, diacetonamine, trimethylamine, glycocine, potassium thiocyanate, cyanuric acid, and orthotoluidine are quite useless. Anisidine and orthotoluidine can also serve as sources from which the organisms obtain their nitrogen.

J. J. S.

Alcoholic Fermentation without Yeast Cells. By EDUARD BUCHNER (*Ber.*, 1897, **30**, 1110—1113. Compare this vol., ii, 154).—The author finds that the aqueous extract loses its fermentative properties when kept for two days at 0°, or for one day at the ordinary temperature. This deterioration of the extract is accompanied by a loss in coagulable albumin, and the deterioration is attributed to the presence of peptonic enzymes. The extract retains its activity much longer in the presence of strong solutions of cane-sugar. When the extract is mixed with its own volume of a 50 per cent. solution of cane-sugar, fermentation continues for 7 days at a moderate temperature, and for 14 days at 0°. That the activity is not due to the presence of plasma particles in the extract is proved by the fact that the activity of the solution is not destroyed by antiseptics, such as chloroform, benzene, sodium arsenite, &c. The extract may also be evaporated to dryness at 30—35° under reduced pressure, and an aqueous solution of the residue is also capable of fermenting cane-sugar. The dried extract may be kept for at least 20 days without losing its active properties. In one instance only was it found possible to precipitate the active substance, *zymase*, by the aid of alcohol.

Well-washed yeast was dried at 37°: one portion, A, was mixed with water and heated to 100°, plate cultures proved that all the cells had been destroyed and yet the solution was capable of fermenting a sterilised cane-sugar solution; the second portion, B, was heated to

140—145° for one hour; this portion, however, was incapable of bringing about fermentation, owing to the destruction of the zymase.

J. J. S.

The Cause of Poisoning by Wall-papers containing Arsenic. By B. Gosio (*Ber.*, 1897, **30**, 1024—1026. Compare this vol., ii, 114). *Mucor mucedo*, *Aspergillus glaucus*, and *A. virens* were the first organisms isolated which were capable of decomposing arsenic compounds. The author finds that *Penicillium brevicaule* is also capable of decomposing all solid arsenic compounds, including arsenical dyes; this reaction is so delicate that the author has used it as a means of detecting arsenic. The nature of the volatile arsenical compounds evolved has not been definitely established, although their strongly poisonous character can be readily shown.

J. J. S.

The Cause of Poisoning by Wall-papers containing Arsenic. By Oskar Emmerling (*Ber.*, 1897, **30**, 1026. Compare previous abstract).—The author states that the volatile arsenical compounds given off by different micro-organisms during the decomposition of solid arsenic compounds is not hydrogen arsenide. Some doubt is also thrown on the poisonous nature of these products.

J. J. S.

Phosphorescence of Wood. By Fr. Kutscher (*Zeit. physiol. Chem.*, 1897, **23**, 109—113).—Most observers agree that the phosphorescence of decomposing wood is due to fungoid growth. This conclusion has been questioned by De Bary. In the present research, De Bary is shown to be wrong. The fungus was isolated, cultivated on gelatin, and other wood infected with it. Some of the characters of the growth are described, although its place in schemes of classification is not decided.

W. D. H.

Reduction of Nitrates. By Pierre P. Dehérain (*Ann. Agron.*, 1897, **23**, 49—79).—A number of experiments were made in which solutions of potassium nitrate were inoculated with straw, fresh manure, horse-dung, and peat manure. The results showed the presence of nitrate-reducing organisms in straw and in fresh manure (compare Bréal, Abstr., 1892, 1259; and 1896, ii, 444), but not in peat manure. The horse-dung contained sufficient to reduce nitrates at 30°, but there was very slight reduction at the ordinary temperature.

The denitrifying organisms develop rapidly in solutions containing starch and potassium nitrate: there is no development in pure nitrate solutions. The organisms will live in starch alone, but in absence of nitrate the starch is only very slowly destroyed. Solutions which reduce nitrates most rapidly contain starch (0·25), potassium nitrate, (0·2) and potassium phosphate (0·01 per cent.).

Experiments with soil showed the presence of denitrifying organisms, and that by adding starch a considerable amount of the nitrates present in the soil could be destroyed. The addition of straw containing denitrifying organisms to soil had very little effect on the nitrates present in the soil.

The amount of nitrogen utilised by the reducing organisms is very slight, nearly the whole of the nitric nitrogen being liberated as gas, chiefly free nitrogen. Reduction takes place more readily in closed

vessels than in the open air, and is retarded by passing air through solutions containing starch and potassium nitrate.

There is no danger of loss of nitrogen by the application of the usual amounts of manure. Reduction of nitrates would only take place when the manure amounted to 400,000—800,000 kilos. per hectare. It is, therefore, quite unnecessary to treat stable manure with sulphuric acid before using it. N. H. J. M.

The Enzyme of Barley which Dissolves Cell-walls. By FRIEDRICH REINITZER (*Zeit. physiol. Chem.*, 1897, **23**, 175—208).—The author failed to obtain cytase, the cell-dissolving enzyme of barley described by Brown and Morris (Trans., 1890, 497). The diastase of germinating barley has, however, the power of dissolving the readily hydrolysible hemicelluloses, which probably have a very widespread distribution in the vegetable kingdom; but many of the hemicelluloses are not attacked by diastase. When these pass into solution as germination proceeds, no doubt some ferment which may be called cytase is at work. W. D. H.

Composition and Analysis of Wheat. By AIMÉ GIRARD (*Compt. rend.*, 1897, **124**, 876—882).—In order to be of value for manufacturing purposes, chemical analyses of wheat should be made, not on the whole grain, but on the products of a mechanical analysis, corresponding as closely as possible with the operations of milling. Two analyses, one of the usable flour, the other of the bye-products, are generally sufficient. On mechanical analysis, four French wheats of 1895 gave: water 14·50 to 15·12, kernel 83·04 to 85·98, germ 1·16 to 1·50, envelope 12·52 to 15·61 = 100. The average weight of a grain was 0·038 to 0·051 gram.

Of substances soluble in water, the proportion in flour is generally given as 10 to 12 per cent. of the weight of the wheat, and they are said to consist of about 50 per cent. of glucose and dextrin. These results are, however, erroneous, and are due to the action of the diastases in the wheat during the somewhat long soaking in water which is generally given for the purpose of extracting the soluble matter. Accurate estimations are obtained by agitating the flour with ice-cold water for about 4 hours; the proportion of soluble matter does not exceed 4 or 5 per cent. and it contains a very small quantity of glucose and no dextrin. It is only by the use of a low temperature that the action of the diastases can be minimised; such antiseptics as could be used are without effect.

When the aqueous solution at 0° is mixed with four times its volume of alcohol of 95° a white, flocculent precipitate is formed, which contains no dextrin but consists of nitrogen compounds (including diastases) together with about 1 per cent. of galactin, the gum corresponding with galactose and described by Müntz. The alcoholic liquid contains no dextrose, but from 1 to 2 per cent. of saccharose.

The ordinary method of estimating gluten is the simplest and most accurate, but it is important that it should be dried at 100—105°, and the drying is facilitated by first coagulating the gluten by immersing it for a few minutes in boiling water. The proportion of glutenin and gliadin in the gluten should be estimated by Fleurent's method (*Compt. rend.*, **123**, 327), since when the ratio differs much from 25 per cent. of

the former, to 75 per cent. of the latter, the flour does not yield bread of such good quality.

Starch is generally estimated by difference or more rarely by conversion into sugar, but direct estimation by washing, collecting on a very fine sieve and drying at 100—105°, is simpler and at least as accurate. For the estimation of fat, crystallisable benzene is preferable to ether.

Analyses of the four French wheats previously referred to gave the following results: Water 14·74 to 15·58; matter soluble in water 3·12 to 4·00 per cent., consisting of glucose 0·09 to 0·21, saccharose 0·86 to 1·70, nitrogen compounds 1·02 to 1·28, galactin, &c., 0·52 to 0·99, inorganic matter 0·22 to 0·36; matter insoluble in water 79·94 to 80·94 per cent., consisting of gluten 7·45 to 8·32, starch 69·88 to 71·22, fat 0·84 to 1·12, inorganic matter 0·20 to 0·40, cellular matter and débris 0·22 to 0·25; acidity in terms of sulphuric acid 0·006 to 0·011. The ratio of glutenin to gliadin varied from 25/62 to 25/87. C. H. B.

Manure Value of Oil Cakes. By L. MALPEAUX (*Ann. Agron.*, 1897, **23**, 28—42).—Field experiments were made in which barley and sugar-beet were grown without manure, with sodium nitrate (300 kilos. per hectare), and with nine different kinds of oil cake (1000 kilos. per hectare). In a second series, superphosphate was applied in addition to the nitrogenous manures, and also to a plot not otherwise manured. Two similar series of pot experiments were also made.

The effect produced by the cakes is chiefly due to the nitrogen they contain. The different cakes vary considerably in value. The use of superphosphate in addition to cake is not necessary when the soil contains over 0·1 per cent. of phosphoric acid. The best time for applying cake is the autumn; when applied in the spring, the results are uncertain, being dependent on climatic conditions. Of the different cakes employed, sesame cake was the most effective: earth nut cake was less favourable, rape cake, cotton cake, and castor-oil cake still less so. This scale of value is, however, not absolute, being based on only one year's results. N. H. J. M.

Bat Guano from Eboli, Salerno. By JULES PARIS (*Ann. Agron.*, 1897, **23**, 47—48).—The sample analysed contained: water 18·02, mineral matter 52·87, and nitrogen (almost entirely as nitrates) 2·996 per cent. The ash, of which 25·61 per cent. was soluble, had the following percentage composition :—

K_2O.	Na_2O.	CaO.	MgO.	Al_2O_3 & Fe_2O_3.	P_2O_5.	Insol. in HCl.
2·08	0·81	13-84	0·18	16·85	20·69	44·69

Of the phosphoric acid, 47·96 per cent. was soluble in ammonium citrate. The ash contained a small amount of copper, and traces of manganese. It is suggested that the presence of copper is due to the bats having eaten insects containing copper (compare Giunti, *Ricerche sulla Diffusione del Rame*, Naples, 1881.) N. H. J. M.

Analytical Chemistry.

Apparatus for Gas Analysis. By OTTO BLEIER (*Ber.*, 1897, 30, 1210—1211. Compare Abstr., 1896, ii, 70; this vol., ii, 280).—The author has improved the gas burette which he formerly described by replacing the upper tap by a three way tap, so that gas can be transferred from the pipette to the burette without either loss or addition.

A. H.

Preparation of Reagents Free from Arsenic. By JOSEF HABERMANN (*Zeit. angw. Chem.*, 1897, 201—202).—Hydrochloric acid is mixed with a little potassium chlorate (0·5 gram per litre is generally sufficient), and the liquid distilled and condensed in a receiver containing an appropriate amount of water; the distillation is stopped when about 75 per cent. of the acid has distilled over. All the arsenic remains in the retort, and the distillate will not contain a trace of it; it contains a small amount of free chlorine, however, which in toxicological investigations is of no consequence.

Ammonia, free from arsenic, may be obtained by adding to the commercial article a little potassium permanganate, heating the mixture in a flask and passing the gas into distilled water.

Ammonium sulphide, free from arsenic, is obtained by passing hydrogen sulphide into the purified ammonia. To obtain the hydrogen sulphide free from arsenic, the excess of moisture is removed, and the gas is then passed first through a tube containing a small quantity of iodine and subsequently through a wash bottle containing water.

L. DE K.

A Simple Method of Quantitative Analysis by Means of the Telephone. By HUGO ERDMANN (*Ber.*, 1897, 30, 1175—1182).—The solubility of sparingly soluble substances has been determined from the electric conductivity of the saturated solutions (Kohlrausch and Rose, Abstr., 1894, ii, 7), and the same property has been utilised by Beckmann to evaluate milk, wine, and beer. Taking advantage of the considerable differences in conductivity exhibited by solutions of potassium chloride, bromide, and iodide, the author has elaborated a method by which mixtures of these electrolytes may be analysed quantitatively by means of the wire-bridge and telephone.

To the extremities of the wire, which are placed in connection through an induction apparatus situated in a neighbouring room, are connected two Arrhenius' resistance cylinders W and W', with the junction of which the sliding-piece communicates through a telephone; in order to eliminate the effect on conductivity produced by temperature, both cylinders are placed in the same vessel containing water. If now a mixture of potassium chloride and bromide is to be analysed, the cylinders are filled with a 1 per cent. solution of the former salt, and the position of minimum disturbance recorded; W' is then refilled with a 1 per cent. solution of potassium bromide, and a fresh observation made. The mixture of unknown composition is afterwards in-

troduced into W', in the form of a 1 per cent. solution, when its conductivity may be compared with that of the pure potassium chloride; the ratio of the resistance of the latter to the resistance of the mixture decreases as the percentage of potassium bromide in the mixture is increased, and the decrease being directly proportional to the rise in percentage of potassium bromide, the amount of the latter salt which is present in the mixture may be calculated.

This method of analysis has been applied to mixtures of potassium chloride with potassium bromide, potassium bromide with potassium iodide, and potassium chloride with potassium iodide, and also to a mixture of potassium sulphate with rubidium sulphate. M. O. F.

Separation of Chlorine and Bromine. By HENRI BAUBIGNY and PAUL RIVALS (*Compt. rend.*, 1897, **124**, 859—862).—It is well known that potassium permanganate does not decompose alkali bromides or chlorides in aqueous solution. If, however, the alkalis are displaced by some other metals, decomposition may take place. Cupric bromide is decomposed by the permanganate at the ordinary temperature with liberation of bromine, but cupric chloride is not affected. In order to separate the two halogens in this way, the carefully neutralised solution of chloride and bromide is mixed with excess of cupric sulphate, and potassium permanganate is added and the liquid allowed to evaporate in a vacuum over potassium hydroxide at the ordinary temperature. A large, flat dish should be used, so that the residual salt forms only a thin film in which very little bromine can be occluded. If necessary, the residue may be moistened with water and again allowed to evaporate under the same conditions. The chlorine is precipitated with silver nitrate containing a considerable proportion of nitric acid, after the permanganate has been reduced with sulphurous acid.

If aluminium sulphate is substituted for cupric sulphate, there is considerable loss of chlorine under the same conditions. C. H. B.

Study of Kjeldahl's Process and its Modifications. By G RIVIÈRE and G. BAILHACHE (*Bull. Soc. Chim.*, 1897, [iii], **15**, 806—811). —The authors employ sodium pyrophosphate in place of the potassium sulphate generally used. A table showing the time occupied by the analysis, and the results obtained by different methods, is given.

M. W. T.

Colorimetric Estimation of Nitrous Acid. By E. RIEGLER (*Zeit. anal. Chem.*, 1897, **36**, 306—307).—A typical solution is prepared by dissolving 0·406 gram of silver nitrite in hot water, adding a small excess of sodium chloride, and diluting to a litre. Of the clear solution, 100 c.c. is again diluted to a litre, and 100 c.c. of this dilution (corresponding with 0·001 gram of N_2O_3) is mixed in a flask with about 0·05 gram of crystallised naphthionic acid, 5—6 drops of concentrated hydrochloric acid, and, after thorough shaking, 30 drops of strong ammonia. The solution to be assayed is treated in like manner, and the rose-red colours compared in a colorimeter. 0·00001 gram of N_2O_3 in 100 c.c. can be estimated by this method. M. J. S.

Estimation of Carbon in Ferro-Chrome. By HARRY BREARLEY and RUDOLF L. LEFFLER (*Chem. News*, 1897, **75**, 241—243).—The pulverised ferro-chrome is mixed with pulverised lead chromate, placed in a boat, and burnt in a current of oxygen in a tube packed with copper oxide; the reaction in the boat, which has to be assisted by heating with a foot blowpipe, takes place with great rapidity at one stage and is sluggish at another; therefore a reservoir is interposed, at the oxygen supply end, to accommodate the rush of gas and to subsequently permit of its steady passage through the tube; moreover, the tube is protected against the great heat by wrapping it first with paper and then with asbestos millboard, the paper leaving a layer of ash that prevents the asbestos fusing to the glass; millboard is also used to prevent the porcelain boat employed from fusing to the tube. Zinc oxide and litharge used instead of lead chromate did not give satisfaction; with copper oxide, the heat has to be greater and the reaction is less violent; but lead dioxide is effective and convenient, for it does not require the aid of a blowpipe flame. D. A. L.

Solubility of Potassium Platinochloride in Alcohol. By M. PÉLIGOT (*Zeit. anal. Chem.*, 1897, **36**, 322; from *Mon. sci.*, [iv], **6**, 872).—One litre of alcohol at 20° dissolves the following amounts of potassium platinochloride:

Strength of alcohol	85	90	95 per cent.
Potassium platinochloride dissolved	0·180	0·100	0·030 gram.

A mixture of 800 c.c. of 95 per cent. alcohol and 200 c.c. of ether dissolves 0·027 gram. These corrections are not applicable to potassium estimations, since the solubility is modified by the presence of sodium platinochloride. M. J. S.

Estimation of Potassium. By HENRY N. WARREN (*Chem. News*, 1897, **75**, 256).—The solution of the alkali chlorides is heated and evaporated to a small bulk with excess of platinic chloride, and then mixed with double the original quantity of a mixture of amylic alcohol and ether in equal proportions. The precipitate is washed with the same mixture, heated to the boiling point with formic acid, and the precipitated platinum washed, dried, and weighed; the percentage of potassium is calculated from this weight. D. A. L.

Testing Sodium Hydrogen Carbonate. By GEORGE LUNGE (*Zeit. angw. Chem.*, 1897, 169—171).—The author communicates a process originated by Sundstrom, and thinks that it may be recommended. The sample is dissolved in cold water and titrated with standard soda, which has been nearly saturated with baryta (so as to be perfectly free from carbonate), until a drop of the liquid gives a brown coloration with silver nitrate. From the results, the excess of carbonic acid present above that required for the normal carbonate can easily be calculated.

Another portion of the sample is then titrated with standard acid, using methyl-orange as indicator. We have then the means for calculating the purity of the salt. L. DE K.

Estimation of Zinc Oxide. By EMILY ASTON and L. NEWTON (*Chem. News*, 1897, **75**, 133—134).—Fresenius states that zinc oxide

when mixed with sulphur, and gradually heated to redness in a current of hydrogen is quantitatively transformed into zinc sulphide. The authors find this to be the case with zinc oxide prepared by ignition from the carbonate, sulphide or sulphate; but with oxide prepared from the nitrate, in the manner set forth below, the result falls short of the theoretical by some 10 per cent., a number that is reduced by very small quantities at a time by repeating the operation, which, in one case, was done above 22 times; but even then the quantity of zinc sulphide did not exceed 96 per cent. of the theoretical. The oxide, that behaved in this manner, was prepared by dissolving practically pure zinc in pure nitric acid, evaporating the solution to dryness, dissolving the residue in water, filtering the solution, treating the filtrate with a few drops of ammonium sulphide, agitating frequently, and again filtering. This solution was then evaporated to dryness, the residue dried at 150°, and ignited first in a blowpipe and then in a muffle.

D. A. L.

Estimation of Manganese in Manganous and Permanganic Solutions. By ANTONIO LONGI and S. CAMILLA (*Gazzetta*, 1897, **27**, i, 97—117).—The authors have re-investigated Volhard's modification (Abstr., 1880, 141) of Gensard's method (*Bull. Soc. Chim.*, [ii], **1**, 88) of estimating manganese in a manganous solution by titrating it with potassium permanganate, when the following reaction occurs: $3MnO + Mn_2O_7 = 5MnO_2$; addition of nitric acid to the solution, as recommended by Volhard, does not clarify it successfully, but this object may be attained by titrating in a solution containing about 0·025 per cent. of manganese and 0·5 per cent. of zinc sulphate. Meinecke's criticisms (*Rep. Anal. Chem.*, 1885, **5**, 1) of Volhard's method are mostly unfounded. The manganous solution containing zinc sulphate is titrated at the boiling temperature with N/10 potassium permanganate solution until a persistent red colour is obtained; the precipitate should settle readily, leaving the supernatant liquid clear. Any adherence of manganese dioxide to the sides of the flask is due to the latter being dirty, and may be prevented by previously washing with a sulphuric acid solution of chromic anhydride. After cooling the titrated solution, a check on the result is obtained by adding potassium iodide and hydrochloric acid, and titrating the liberated iodine with thiosulphate; this is the more necessary when much chromium salts are present, since these obscure the end reaction with permanganate, and in such a case it is advisable to filter off the manganese dioxide through a filter paper before treating it with potassium iodide.

Permanganates may be determined by titration with a manganous salt in neutral solution, or in one slightly acidified with acetic or nitric acid. The estimations may be performed in presence of chromic acid, nickel, cobalt, and lead.

W. J. P.

Separation of Nickel from Cobalt and Iron, and of Cobalt from Aluminium. By EUGENIO PIÑERÚA (*Compt. rend.*, 1897, **124**, 862—863).—Nickel chloride is insoluble at a low temperature in ether saturated with hydrogen chloride, whereas cobalt and ferric chlorides dissolve readily. In order to utilise these facts for analytical purposes, the metals are converted into chlorides, which are dissolved

in the smallest possible quantity of water, a moderately large quantity of a mixture of equal volumes of concentrated hydrochloric acid, and ordinary, or preferably dry, ether is added, and a current of hydrogen chloride is passed into the liquid, which is cooled in a mixture of ice and salt. The yellow precipitate of nickel chloride is washed with ether saturated with hydrogen chloride, at first by decantation and afterwards on a filter.

The so-called pure compounds of nickel and cobalt are generally more or less impure; the former contain cobalt and iron, and the latter contain nickel and iron.

When applying this method to the separation of nickel from iron, the precipitate must be very well washed, redissolved in water, and the operation repeated several times in order to eliminate the iron which the nickel chloride obstinately retains.

Cobalt can be separated from aluminium in the same way, the aluminium chloride being precipitated. C. H. B.

Separations with Alkali Acetates. By HARRY BREARLEY (*Chem. News*, 1897, **75**, 253—254).—The author shows that the quantity of sodium or ammonium acetate required to completely precipitate the iron from "neutralised" solutions of ferric chloride (that is, solutions of ferric hydroxide in ferric chloride) is diminished by the proportion of hydroxide, and increased by the amount of free acetic acid in solution. Incidentally, it is observed that small quantities of iron may be removed from solutions by an asbestos filter, and that salts of the alkalis exert to a certain extent a neutralising effect, the chlorides being more active than the nitrates in this respect. D. A. L.

Estimation of Titanic Acid. By J. JAMES MORGAN (*Chem. News*, 1897, **75**, 134).—The author approves of the following combination of the methods of Arnold and of Blair. The ore, mixed with 1 gram of ammonium phosphate in solution in a small quantity of water, is dissolved in hydrochloric acid, and the solution evaporated to dryness. The residue is well dried ("well baked"), extracted with hydrochloric acid, the solution diluted, and the residue, which contains all the titanic acid as phosphotitanate of iron, is collected, washed free from iron salts with hot dilute hydrochloric acid and cold water, and after drying is fused in a platinum crucible with ten times its weight of potassium carbonate. The mass is treated, and washed carefully, with hot water, and the dried residue is fused in a platinum crucible, at a low red heat, for half an hour with about 6 grams of potassium hydrogen sulphate. When cold, the mass is treated with 10 c.c. of hydrochloric acid and 50 c.c. of sulphurous acid, filtered, and washed with hot water; 20 grams of sodium acetate in aqueous solution is added to the solution, which is then boiled for a few minutes with one-sixth of its volume of acetic acid; the precipitate is washed, dried, ignited, and weighed as TiO_2.

Pig iron, without addition of ammonium phosphate when the phosphorus is high and the titanium low, is dissolved in nitric acid (sp. gr. = 1·20), and the solution evaporated to dryness; the residue is then thoroughly dried, dissolved in hydrochloric acid, and the drying repeated; finally, the mass is again dissolved in hydrochloric acid, and the solution diluted, filtered and treated as above. D. A. L.

Estimation of Sugar. By EDUARD PFLÜGER (*Pflüger's Archiv*, 1897, **66**, 635—640).—See this vol., ii, 378.

Lactic Acid. By FERDINAND ULZER and HEINRICH SEIDEL (*Monatsh.*, 1897, **18**, 138—141).—The purity of a sample of lactic acid can be estimated conveniently by dissolving about 1 gram of the sample in 100 c.c. of water containing 3 grams of potassium hydroxide; adding gradually, and with continual shaking, a 5 per cent. solution of potassium permanganate until the liquid has no longer a green, but a bluish-black colour, boiling (when the bluish-black colour must still remain), decolorising by the addition of hydrogen peroxide or sulphurous acid, filtering, acidifying with dilute sulphuric acid, and titrating the oxalic acid with standard permanganate solution. It is assumed that the lactic acid has been oxidised in accordance with the equation $C_3H_6O_3 + 5O = C_2H_2O_4 + 2H_2O + CO_2$. In this way, a sample of Merck's "chemically pure" acid was found to contain 90·13 per cent. $C_3H_6O_3$; by boiling with excess of standard potassium hydroxide and titrating the excess, 89·50 was found. The same sample gave only 74·05 per cent. when titrated with potassium hydroxide in the cold, so that it must have contained a large amount of lactone-anhydride; a sample of commercial acid was found to contain an even larger amount.

Palm's method of estimating lactic acid (Abstr., 1887, 307), by precipitating with lead acetate and alcoholic ammonia, and weighing the precipitate as $3PbO,2C_3H_6O_3$, after drying it at 100°, does not give concordant results. C. F. B.

Estimation of Added Water in Milk by the Freezing Point Method. By HARTOG J. HAMBURGER (*Rec. trav. Chim.*, 1896, **15**, 349—355. Compare Abstr., 1896, ii, 550).—The mean lowering of the freezing point of numerous samples of milk examined by the author is 0·561°, the lowering of the freezing points varying between 0·574 and 0·556. Not only can the method be used for detecting added water, but also for estimating the amount, amounts beyond 3 per cent. being easily estimated. J. J. S.

Testing American Lard. By VON RAUMER (*Zeit. angw. Chem.*, 1897, 210—215, 247—254).—The author has taken the iodine absorption of lards after removing the bulk of the lard-stearin by means of amylic alcohol, but has not obtained satisfactory results. For instance, a mixture of 75 parts of tallow and 25 parts of cotton-seed oil still came within the limits of genuine lard.

The only good method for the detection of cotton-seed oil in lard is the iodine absorption figure of the liquid fatty acids, which for European lards does not exceed 94, but unfortunately American lards which are undoubtedly genuine often give a figure even as high as 104.

L. DE K.

Assay of Commercial Xylidines. By WILHELM VAUBEL (*Zeit. anal. Chem.*, 1897, **36**, 285—289).—Commercial xylidines contain five isomerides, namely, those having the 1 : 2 : 4, 1 : 2 : 3, 1 : 3 : 4, 1 : 3 : 2, and 1 : 4 : 2 constitutions. Of these, the 1 : 3 : 4 and 1 : 4 : 2 compounds

usually predominate, the former being technically the most important of the five. A rough assay may be made by mixing 100 grams of the substance with an equal weight of glacial acetic acid. Hydrochloric acid is sometimes used, but the results are less trustworthy. After 24 hours, the precipitate is collected on a suction filter, air dried, and weighed. It consists mainly of the acetate of 1 : 3 : 4-xylidine, which is practically insoluble in acetic acid, but it is liable to be contaminated to a considerable extent with the acetate of 1 : 2 : 4-xylidine, and with acetyl derivatives of all the isomerides. The acetate of 1 : 3 : 2-xylidine is freely soluble. All the acetyl derivatives, when treated with nascent bromine, absorb one atom of bromine, as do also the two metaxylidines, whereas the ortho- and para-xylidines absorb two atoms. If therefore the acetyl derivatives are hydrolysed before bromination, which may be accomplished by boiling for 10 minutes with hydrochloric acid, a titration of the bases with hypobromite and acid will afford the data for calculating how much of the ortho- and para-xylidines have been precipitated with the asymmetric metaxylidine.

M. J. S.

Estimation of Urea in Urine. By E. RIEGLER (*J. Pharm.*, 1897, [vi], 5, 30—31).—One c.c. of urine is mixed with 2 c.c. of Millon's reagent (10 c.c. of mercury dissolved in 130 c.c. of nitric acid of sp. gr. 1·4, and then diluted with 140 c.c. of water), and the liquid boiled. The amount of urea present is deduced from the quantity of nitrogen and carbonic anhydride evolved. An apparatus is described and a table is given for the calculation of results. M. W. T.

Differentiation of the Alkaloids by means of their Microcrystalline Precipitates. By VADAM (*J. Pharm.*, 1897, [vi], 5, 100—105).—The author describes the appearance and mode of formation of the crystalline precipitates which are formed on adding the various reagents described in a previous paper (this vol., ii, 292) to the more common alkaloids. M. W. T.

Estimation of Caffeine. By W. A. PUCKNER (*J. Amer. Chem. Soc.*, 1896, 18, 978—981).—The author confirms Allen's statement that caffeine may be removed from acid solutions by means of chloroform, but he finds that the larger the amount of free acid the more difficult it is to extract the alkaloid. In the first set of experiments, a quantity of caffeine varying from 0·1285 to 0·4416 gram was dissolved in 50 c.c. of 1 per cent. sulphuric acid, and treated first with 25 and then three times in succession with 10 c.c. of chloroform, when it was found that the alkaloid had all but completely passed into the chloroform.

In the second experiment, 1·0137 gram of caffeine was dissolved in 60 c.c. of 10 per cent. sulphuric acid, and it now required five successive extractions with 25 c.c. of chloroform before the bulk of the alkaloid had been extracted, whilst four more treatments with 25 c.c. of chloroform each were necessary to remove the last traces. L. DE K.

Separation of Codeine and Morphine. By L. FOUQUET (*J. Pharm.*, 1897, [vi], 5, 49—50).—Codeine and morphine may be easily

separated by taking advantage of their relative solubilities in anisoil; the respective solubilities in parts by weight per 100 being

Temperature.	9°	16°	32°	100°	150°
Morphine	Insoluble	Insoluble	Insoluble	0·95	4·80
Codeine	7·80	15·28	—	164·00	—

Codeine, when once crystallised from anisoil, is soluble at 0° to the extent of 10·75 parts per 100. M. W. T.

Estimation of Morphine in Opium and Opiates. By ALEXANDRE GRANDVAL and HENRI LAJOUX (*J. Pharm.*, 1897, [vi], **5**, 153—158).—A detailed account of the method of procedure is given. The morphine and narcotine are precipitated from alcoholic solution by means of ammonia, and the narcotine subsequently removed by treating the mixture of the two alkaloids with chloroform.

If the precipitate of the mixed alkaloid contains much resinous matter, it should be treated with hydrochloric acid and water to dissolve the alkaloids, filtered, the filtrate nearly neutralised, and evaporated to a small bulk. The impurities may now be filtered off, and the morphine and narcotine precipitated from the solution as before.

M. W. T.

Testing Quinine. By OSWALD HESSE (*Arch. Pharm.*, 1897, **235**, 114—125).—Polemical. A reply to Kubli (this vol., ii, 168). Compare Abstr., 1896, ii, 550. J. J. S.

Estimation of Quinine. By DAVID HOWARD (*Pharm. J. Trans.*, [iv], **3**, 505—507).—The paper deals mainly with small, but essential, points in the ordinary methods of testing the purity of commercial quinine sulphate. The author remarks that it is, perhaps, not wise to insist on the use of a chemically pure salt in pharmacy, as the other cinchona alkaloids are not only innocuous, but have the same therapeutic effects as quinine, although in a lower degree.

The most common impurity is cinchonidine sulphate, and this is best tested for by crystallising the bulk of the quinine as acid sulphate. The mother liquor is then shaken with ammonia and ether, which will cause the greater portion of the cinchonidine to crystallise out. This, according to the author's experience, contains, however, a notable amount of quinine, from which it may be freed by dissolving it in absolute alcohol and adding 2·1 c.c. of 50 per cent. sulphuric acid for every gram of the alkaloid present. The cinchonidine now almost entirely crystallises as sulphate and may be collected as such. A process is given to recover the little cinchonidine still dissolved by the ether, but this the author considers unnecessary in practice. The ethereal solution is, however, likely to contain hydroquinine, an alkaloid not generally suspected, but occurring lately, sometimes to the extent of 4 per cent., in commercial samples of quinine sulphate. The ethereal solution is evaporated to dryness, the residue dissolved in dilute sulphuric acid, cooled to zero, and a 4 per cent. solution of potassium permanganate added until the reddish colour is but slowly discharged. After filtering from the precipitated manganese oxide, the liquid is rendered alkaline with ammonia and agitated with

ether. This is then shaken with dilute sulphuric acid, which dissolves the hydroquinine, and the latter is obtained as solid sulphate by neutralising the solution with soda.

The tests for the purity of quinine sulphate provided in the German, Italian, American, and Dutch pharmacopœias are given; these are all based on the insolubility of the inferior cinchona alkaloids in ammonia and the comparatively large solubility of quinine in that reagent. When applying the ammonia test, the bulk of the quinine sulphate must be first removed by recrystallisation, but the author observes that it is not possible to entirely prevent the formation of a double compound of quinine sulphate and cinchonidine sulphate, which is only slightly soluble. The best results are obtained by filtering off when the liquid has cooled down to 50°. L. DE K.

Detection of Ground Olive Stones in Pepper. By DOMENICO MARTELLI (*Staz. Sper. Agrar.*, 1895, **28**, 53—56. Compare Gillet, Abstr., 1889, 88; Chevreau, *Rep. Pharm.*, 1889, **45**, 203; Jumeau, *Jour. Pharm.*, 1889, [v], **20**, 442).—The pepper (0·5 gram) is placed in a flat porcelain dish, covered with a phloroglucinol solution, prepared by digesting phloroglucinol for a day or two with 50—60 parts of hydrogen chloride, sp. gr. = 1·1, and carefully heated until acid fumes begin to be evolved. In presence of olive stones, or similar substances (shells of almonds, walnuts, &c.), an intense cherry-red coloration is produced, readily distinguished from the yellow or brownish-red coloration acquired by pepper. When water is added and then poured off, a violet-red powder, consisting almost entirely of dyed olive stones, or other impurity, remains.

By employing mixtures of pure pepper and ground olive stones, it was found possible to detect 10 per cent. of impurity without using a microscope. N. H. J. M.

Detection of Horse Flesh. By W. NIEBEL (*Zeit. anal. Chem.*, 1897, **36**, 267—268; from *Zeit. Fleisch und Milchhygiene*, **1**, 185, 210; **5**, 86, 130).—Horse flesh differs from beef, veal, pork, and mutton in containing a much larger proportion of glycogen and dextrose. To estimate the glycogen, 50 grams of the flesh is digested on the water bath for 6—8 hours with 200 c.c. of potash solution (1·5—2 grams of potash) and the estimation made by the method of Brücke and Külz (Abstr., 1872, 83; *Zeit. anal. Chem.*, **22**, 299), or, if starch or dextrin be present, by that of Landwehr (Abstr., 1884, 1287). For the dextrose estimation, 100 grams of finely chopped flesh is thrice extracted by boiling for 2 minutes with 500 c.c. of water, and the decolorised extract evaporated to 100 c.c. and titrated with Fehling's solution. If both constituents are calculated as dextrose (162 parts of glycogen = 180 parts of dextrose), values ranging from 3·8 to 6·19 per cent. are obtained for horse flesh, whilst the upper limit for the other kinds of flesh may be taken as 1 per cent., both being calculated on the dry, fat-free substance. The presence of liver, or the flesh of very young calves (both often employed in sausages), raises the normal limit. The pale colour of young veal, and the characteristic brownish-red colour of horse flesh, will assist in distinguishing these cases. M. J. S.

General and Physical Chemistry.

Absorption Spectra of some Compounds in the Gaseous and Liquid States. By J. PAUER (*Chem. Centr.*, 1896, i, 1122; from *Ber. Physikal.-Med. Soc. Erlangen*, **27**, 120—126).—The substances examined were benzene, toluene, the xylenes, ethylbenzene, chloro-, bromo-, iodo-, nitro-, amido-, azo-, and amidoazo-benzene; carbon bisulphide, pyridine, thiophen, anthracene, and naphthalene. Their absorption spectra are in the ultra-violet, and were therefore in each case photographed. All the compounds in the liquid state, or in solutions of suitable concentration, give rise to absorption bands near the cadmium lines 17—20 (Mascart's definition). The absorption spectra of the same substance in solution in different solvents show a displacement towards the red which increases with the refractive index or the dispersion of the solvent. The absorption spectra of the vapours consist of lines, or groups of lines, which form one or more bands as the substance passes from the gaseous to the liquid state. The position of the bands for the liquid is always nearer the red than that of the lines or groups of lines, for the vapour.

The influence of constitution on the absorption in the case of the benzene derivatives was not found to follow any regular course. The character of the absorption alters entirely with the substitution of different hydrogen atoms. Nitrobenzene and iodobenzene in the gaseous state give rise to no lines whatever. Benzene, naphthalene, and anthracene in solution each give four bands, which lie nearer to the red the greater the molecular weight of the compound. The substitution of N for CH entirely alters the character of the benzene spectrum. The absorption in the case of benzene and anthracene is very intense, so that even traces of the vapour of the former in admixture with air could be detected. H. C.

Internal Resistance of Galvanic Cells. By ERNST HAAGN (*Zeit. physikal. Chem.*, 1897, **23**, 97—122).—The author describes a method for the determination of the internal resistance of cells which is fundamentally similar to the Wheatstone bridge method for the comparison of the capacities of condensers, the known ratio of the capacities giving the ratio of the resistances. The availability of the method for various classes of cells is first proved by comparison of the results obtained with those obtained by other methods. The experiments afterwards show that the internal resistance of cells during electrolysis is quite independent of the current strength or current density. The slight variations which were found to occur are traceable to alterations in the concentration of the solutions. In the case of accumulators, during discharge the resistance at first slowly increases, the rate of increase being more rapid towards the end; whilst during the charging of the cell the reverse changes occur, the resistance at first diminishing rapidly and afterwards more slowly. The cause of this variation is partly the

change in concentration of the sulphuric acid, and partly alteration of the surface of the lead plates. L. M. J.

Theory of Lead Accumulators. By C. LIEBENOFF (*Chem. Centr.*, 1896, ii, 409; from *Zeit. Electrotechn. und Electrochem.*, 1896, 2, 653—655).—Experiments have been made by the author with the object of proving the existence of lead dioxide in the ionic condition, as required by his theory of lead accumulators (this vol., ii, 239). In a vessel which contained a normal solution of a caustic alkali saturated with lead oxide, three cylinders, the lower ends of which were closed membranes, were placed, and these were filled with normal alkali to the level of the solution in the containing vessel. Electrodes were placed in the first and third cylinders, the centre one serving for the estimation of the lead entering the cylinders by diffusion. After a current had been passed for some time, lead was found in quantity round the positive electrode, but was practically absent at the negative electrode. The compound $Pb(OK)_2$ gives, therefore, the ions $2\overset{+}{K}$ and $\overset{--}{PbO_2}$. This result was confirmed by other experiments. H. C.

Electrolytic Decomposition of Aqueous Solutions. By WALTHER NERNST (*Ber.*, 1897, 30, 1547—1563).—In a lecture before the German Chemical Society, the author reviews the present position of the question of the chemical mechanism of the electrolytic decomposition of aqueous solutions. The author's method (Abstr., 1889, 1095) of calculating the potential difference between a metal and a solution, from the solution pressure of the metal and the osmotic pressure of the solution, is first described, and it is pointed out that the E.M.F. of the galvanic cell formed by combination of two different electrodes is thus readily obtained. By what is practically a reversal of this process, Le Blanc (Abstr., 1891, 1405) obtains the minimum value of the E.M.F. necessary to produce sensible electrolysis in any given solution. The want of agreement between the numbers obtained in practice and those which the theory would predict in certain cases, leads Le Blanc to the view that water sometimes plays a primary part in electrolysis, and is directly decomposed by the current. The E.M.F. necessary to effect this result is according to Le Blanc's measurements 1·68 volt., but from Smale's work on gas batteries (Abstr., 1894, ii, 436) the maximum value should be 1·08 volt. From measurements made in the author's laboratory by Glaser, it appears that a primary decomposition of water can be effected in the case of sulphuric acid and potassium hydroxide solutions with an E.M.F. of 1·08 volts., if the oxygen separates on a large platinised electrode. The point 1·68 volt. is in these cases, however, also characterised by some further decomposition in the solutions. The suggestion is made that water not only dissociates into the ions OH and H, but also into H, H and O, and that the lower E.M.F. is that under which separation of the latter ions takes place, whilst the higher E.M.F. gives rise to separation of the hydroxyl and hydrogen ions.

In the following table, the pressures (in volts.) required for the separation of certain cations and anions from solutions of normal concentration are given:

Cations.		Anions.	
Ag	−0·78	I	0·52
Cu	−0·34	Br	0·94
H	0·0	O	1·08
Pb	+0·17	Cl	1·31
Cd	+0·38	OH	1·68
Zn	+0·74	SO_4	1·9
		HSO_4	2·6

The hydrogen value is taken as zero, as it is evident that an arbitrary value has to be assigned to one of the terms. From this table it is possible to calculate the E.M.F. required for the electrolysis of normal solutions of salts of any of these ions; for zinc bromide, for instance, we get $0·74 + 0·94 = 1·68$ volt. It is further evident that these values indicate the possibility of separating certain ions electrolytically, as has been done by Freudenberg (Abstr., 1893, ii, 506). A large number of other conclusions with reference to chemical action in solution may be drawn from this table, as, for example, for the displacement of one ion by another. It must, however, be remembered that the pressures form only one factor in such changes, and that ionic concentration must also be taken into consideration. H. C.

Determination of Osmotic Pressure by Means of Vapour Pressure Measurements. By ARTHUR A. NOYES and CHARLES G. ABBOT (*Zeit. physikal. Chem.*, 1897, **23**, 56—77).—By observations of the vapour pressure of a solution, the osmotic work is directly obtained. The authors deduce an expression for the osmotic pressure. $P = (1 + \frac{P}{2}k)\frac{s_0}{M}\int_p^{p_0} vdp - (p_0 - p)$ where P is osmotic pressure and p the vapour pressure of the solution; p_0 is the vapour pressure, s_0 the density, v the gaseous molecular volume, M molecular weight, and k compressibility of the solvent. This expression, by neglecting the small terms $\frac{P}{2}k$ and $p_0 - p$ reduces to $P = \frac{s_0}{M}\int_p^{p_0} vdp$, and gives for the osmotic work $\pi = Pv_0/(1 + \frac{P}{2}k)$ where v_0 is molecular volume of the solvent. As k is very small, the osmotic work is hence approximately proportional to the osmotic pressure, and relations deduced from the former hold also for the latter. The authors then describe a series of very careful determinations of the osmotic pressure in the case of ethereal solutions of naphthalene and azobenzene. The vapour pressure of the solution was determined by the dynamical method, the liquid being kept boiling at a temperature of 12·9°, a form of electrical resistance thermometer being employed. The vapour pressure of the pure ether was obtained from Ramsay and Young's numbers (*Phil. Trans.*, 1887, **178**, 63), the physical constants of the liquid employed agreeing exceeding closely with those given by Ramsay. The values for the osmotic pressure and the product, (pressure) × (volume of solutions containing the gram molecular weight) is given in the accompanying table.

Concentration.	*P.* (naphthalen).	*Pv.*	*P.* azobenzene.	*Pv.*
0·01	1·562	27·93	0·958	24·35
0·02	2·942	26·46	1·900	24·29
0·03	4·293	25·91	2·773	23·77
0·05	6·875	25·21	4·620	24·04
0·07	9·357	24·83	6·349	23·87
0·10	12·87	24·35	8·858	23·73
0·13	16·27	24·11	11·28	23·64
0·16	19·55	23·94	13·66	23·66
0·20	23·79	23·84	16·71	23·69
0·24	27·80	23·73	19·62	23·67

It is clear that the values agree very closely with those of a perfect gas at equal concentrations; the gas constant for hydrogen at 12·9 being 24·27, and the van't Hoff law regarding the equality of pressures in the gaseous state and solution is found valid for both compounds. L. M. J.

Saturated Solution of Magnesium Chloride and Potassium Sulphate, or of Magnesium Sulphate and Potassium Chloride. By RICHARD LÖWENHERZ (*Zeit. physikal. Chem.*, 1897, **23**, 95—96).—The composition of the solutions of the above salts at 25°, previously given by the author (Abstr., 1894, ii, 273), was incorrect, owing to the fact that the solutions were not previously heated above this temperature and allowed to cool, a precaution necessary owing to the slight solubility of the potassium salt in the magnesium solution (Abstr., 1894, ii, 273). L. M. J.

Study of Water Solutions of some of the Alums. By HARRY C. JONES and E. MACKAY (*Amer. Chem. J.*, 1897, **19**, 83—118).—The alums, in dilute solution, have a conductivity which is almost exactly the mean of the conductivities of their constituents, from which it follows that the complex alum molecules are broken down completely in such solutions into the molecules of the simpler sulphates, and that these simpler molecules dissociate as if alone, barring the effect on the dissociation produced when the solutions are not isohydric. In concentrated solutions, the alums show a conductivity less than the mean of the conductivities of their constituents. The difference becomes more marked as the concentration increases, and is of the same order as that observed for other double sulphates. It is much greater than that found in the case of mixtures of sulphates incapable of yielding a double salt. This must be regarded as evidence that the alums are partially undecomposed into the constituent molecules in such solutions, or that the dissociation into the simple ions into which the single sulphates break down is not complete. The magnitude of the difference for potassium chromium alum, as compared with the aluminium alums, affords strong evidence that this alum at least exists as such in moderately concentrated solutions. The freezing point determinations confirm the evidence from the conductivity, that the alum molecules exist to some extent in the more concentrated solutions. H. C.

Use of the Mass-action Law in the Examination of Organic Additive Products. The Reaction between Picric Acid and β-Naphthol in Aqueous Solution. By BASIL B. KURILOFF (*Zeit. physikal. Chem.*, 1897, **23**, 90—94).—If to a saturated solution of β-naphthol, picric acid is added, the solubility of the former increases owing to the formation of an additive product of the two compounds. Hence, if the solubility of the β-naphthol is represented by a in gram-molecules, and by c after addition of b gram-molecules of picric acid, then $c-a=$ the number of gram-molecules of the β-naphthol picrate and $b-(c-a)$ the number of free molecules of picric acid, so that the equilibrium constant is hence given by the equation $k(c-a)=a(b-c+a)$. The estimation of the β-naphthol was made by the method indicated by Küster (Abstr., 1894, ii, 432), and although the picric acid was found to interfere with the estimation, this was avoided by the use of a suitable quantity of sodium hydroxide. The values then calculated from different experiments for k gave very fair agreement, that is, within about 10 per cent. of the mean.

The results were calculated without regard to differences in dissociation of the naphthol picrate and picric acid; that is, on the assumption that they are equally dissociated, this being shown to be valid by conductivity determinations. L. M. J.

The Transition of Seignette Salt and of the Corresponding Ammonium Compound. By J. DOCTERS VAN LEEUWEN (*Zeit. physikal. Chem.*, 1897, **23**, 33—55).—The transition temperatures of sodium and potassium racemates and of Scacchis salt had been previously determined (Abstr., 1895, ii, 380 and 485), and the author therefore extended these observations to the sodium potassium and sodium ammonium tartrates. Rochelle salt, on evaporation, first deposits sodium tartrate, indicating a decomposition into the sodium and potassium compounds. The transition temperature for this change was determined for the dry salt by the dilatometric method, and found to be about 55°, the change being represented by the equation $2NaKC_4H_4O_6,4H_2O \gtrless 0{\cdot}54Na_2C_4H_4O_6,2H_2O + 0{\cdot}20K_2C_4H_4O_6,\frac{1}{2}H_2O + 6{\cdot}8H_2O$; $0{\cdot}46Na_2C_4H_4O_6$; $0{\cdot}80K_2C_4H_4O_6$ (saturated solution). The experimental numbers and diagrams are given for the solubility relations in the case of solutions of Rochelle salt, mixed tartrates, Rochelle salt and potassium tartrate : Rochelle salt and sodium tartrate.

In the latter case, at temperatures above 40°, the number of molecules of dissolved potassium tartrate exceeded that of sodium tartrate, indicating the splitting-up of the Rochelle salt. Above 40°, therefore, a saturated solution of Rochelle salt deposits crystals of a mixture of the salt with sodium tartrate, and above 55°, a mixture of the two simple tartrates. With sodium ammonium tartrate, the decomposition takes place according to the equation

$$2NaNH_4C_4H_4O_6,4H_2O \gtrless Na_2C_4H_4O_6,2H_2O + (NH_4)_2C_4H_4O_6 + 6H_2O,$$

the transition temperature as obtained by both dilatometric and tensimetric methods being about 58·5—59°. By measurement of the ratios of the vapour tension of the salt to that of water at different temperatures, the heat of combination with water is obtained by the expression $q=2T_1T_2/(T_1-T_2)\cdot \log F_1/F_2$ where F_1 and F_2 are the above ratios at

the absolute temperatures T_1 and T_2. In the case of Rochelle salt, the values so obtained vary from 2245 to 2527 Cal. (18—31°), and agree well with the value 2373 calculated from the known heats of solution of the tartrates. During the work, the author obtained sodium tartrate with $2H_2O$, in the form of a hard, glassy mass melting at 60°.

L. M. J.

Influence of Pressure on the Velocity of Reactions in Homogeneous Fluid Systems. By A. BOGOJAWLENSKY and GUSTAV TAMMANN (*Zeit. physikal. Chem.*, 1897, **23**, 13—23).—The effect of pressure on the velocity of a reaction is given by the expression $\frac{dk}{dp} = \gamma\left(m'_2\frac{dm'}{dp} + m'_1\frac{dm'_2}{dp}\right)$ where m'_1 and m'_2 are the active masses of the reacting compounds. The alteration of the active mass may be calculated in the case of electrolytes; for non-electrolytes, the influence of pressure on the active mass is proportional to the concentration of the compound. It hence follows that, in reactions between strongly dissociated compounds and non-electrolytes, the percentage pressure change of velocity is independent of the concentration of the electrolyte; Stern (this vol., ii, 92) found the velocity increased slightly with the concentration.

By variation of the non-electrolyte, the influence of pressure on the absolute velocity is proportional to the concentration. Its influence hence on the velocity constant is independent of the concentration results in accord with the experiments of Stern. As the volume change decreases up to 50° in aqueous solutions, the temperature coefficient of the pressure change is negative for aqueous solutions, but may be positive or negative with other solvents, a result in accord with Stern's experiments. The effect also varies with the nature of the electrolyte. Thus the increase of velocity by a pressure of 500 atmospheres is 14 per cent. higher in the case of the hydrolysis of methylic acetate by acetic acid than the case of the similar reaction with hydrochloric acid, the increase in dissociation being 9 per cent. greater. The pressure effect for weak bases was also studied by means of the hydrolysis of methylic acetate by ammonium hydroxide, the velocity being doubled by a pressure of about 2000 atmospheres. The effect on weak bases and acids is hence greater than on the stronger compounds, but the pressure at which equal velocities would obtain is too high to be calculated by extrapolation.

L. M. J.

Velocity of the Hydrolytic Decomposition of Carbonyl Sulphide. By GUSTAV BUCHBÖCK (*Zeit. physikal. Chem.*, 1897, **23**, 123—156).—Carbonyl sulphide decomposes in the presence of water with the formation of carbonic anhydride and hydrogen sulphide, $COS + H_2O = CO_2 + H_2S$, and the author endeavoured to investigate the velocity of the reaction and the effect of various chemically inactive compounds. The extent of the decomposition was determined by the addition of iodine and titration of the excess by sodium thiosulphate; that of the total sulphide by decomposition by alkali, acidification and subsequent iodine titration. For an irreversible reaction, the equation $\frac{dx}{dt} = k(C-x)(A-x)$ should obtain where x is the concentration of de-

composed sulphide and C and A that of undecomposed sulphide and water respectively, this reducing with excess of water to $dx/dt = K(A - x)$. The first set of experiments on the velocity of decomposition by means of water gave a constant value for K, so that the reverse action does not obtain, neither have the products any influence on the velocity. The velocity of decomposition in the presence of acids was next determined, and it was found that the velocity decreases on the additions of acids, the decrease being greater for the more highly dissociated acids, and increasing with the concentration. Monochloracetic acid, however, caused a very slight increase of velocity, and metallic salts in many cases also cause an increase. For a series of allied salts the velocity increases with the atomic weight of the metal, so that it appears as a periodic function of the atomic weight, and may be approximately calculated as an additive function of the anion and cation. The author suggests that the decomposition may be represented by $COS + \overset{+}{H} + \overset{-}{O}H \leftrightarrows SH{\cdot}CO{\cdot}OH$ and then $SH{\cdot}CO{\cdot}OH = H_2S + CO_2$, in which the quantity of the thiocarbonic acid is always proportional to the carbonyl sulphide, so that the alterations of velocity are those of the second reaction. The effect of the salts on the velocity and their internal friction were compared, and although for the metallic salts a parallelism appears to exist, this breaks down if the acids are included.

The effects of carbamide and glycerol were also determined, both compounds causing an acceleration.

The effect of temperature was also investigated, and found to be well represented by the van't Hoff equation, $\log K = B - A/T$ where T is the absolute temperature and A and B are constants. L. M. J.

Study of Atomic Weights. By JOHANNES R. RYDBERG (*Zeit. anorg. Chem.*, 1897, **14**, 66—102).—The author regards the atomic weights of the elements as forming a discontinuous series of numbers, which are not multiples of the atomic weight of hydrogen, although in the case of those elements which have a lower atomic weight than 56, this condition is more nearly fulfilled than could be accounted for by chance coincidence. The higher atomic weights do not, however, approximate in any special manner to whole numbers. The smaller atomic weights P may be regarded as built up of a whole number N and a small fractional number D, so that $P = N + D$. For elements of uneven valency, N is of the form $4n - 1$, and for elements of even valency of the form $4n$, where n is a whole number. Exceptions to this rule are afforded by nitrogen, scandium, and beryllium. The properties of the elements are periodic functions of the values of n. The values of D are periodic functions of the n values. The twin-elements of Lorenz (Abstr., 1896, ii, 639) may be defined as elements which have the same n value and whose N values differ only by unity. This definition would include a number of twin-elements not given by Lorenz, as Nb – Mo, Rh – Pd, Ir – Pt, and Tl – Pb.

RICHARD LORENZ (*ibid.*, 1897, **14**, 103—105), in a note on the preceding paper, calls attention to his definition of twin-elements (*loc. cit.*), and points out that this mode of classification is based on the above definition, and not on a mere approximation in the values of the atomic weights of the similar elements. H. C.

A Graphic Representation of the Periodic System of the Elements. By E. LOEW (*Zeit. physikal. Chem.*, 1897, **23**, 1—12).—The author represents the system of elements by points upon an archimedean spiral in which $v = \phi = \sqrt{w}$, where w is the atomic weight, v the radius vector, and ϕ the polar angle. When this is done, certain allied elements fall very nearly at opposite ends of the same radius, that is, differ in position by π, for example, copper and sodium, magnesium and zinc, phosphorus, and arsenic. If the spiral be divided by a straight line through the origin, it forms segments containing groups of elements of which the corresponding members form a natural group, for example, phosphorus arsenic, antimony and bismuth. Of the last groups, the consecutive members differ very nearly by $\pi/2$ in position, and assuming this to be the true difference, the theoretical positions of the elements are obtained and found to differ but slightly from the previous values, in many cases, the differences being within the probable errors of the atomic weights. The series thus obtained represented the whole system as situated on vectors, each differing from the preceding by $\pi/16$. The vectors for elements of the same family differ by π, and those of a subsidiary allied family differ by $\pi/2$, thus lithium, potassium, rubidium, and cæsium form a family with, at $\pi/2$ intervals, sodium, copper, silver, and gold. The spiral shows certain gaps which may be filled, notably for a whole group between the chlorine and potassium groups. Helium falls in the same group as aluminium, whilst argon and fluorine are classified with the iron and platinum group. L. M. J.

Chemical Proportions. II. By F. WALD (*Zeit. physikal. Chem.*, 1897, **23**, 78—89.)—The author considering that his previous paper (this vol., ii, 311) has been very largely misunderstood, endeavours to give a further explanation of it, and to remove the misunderstanding. He gives an account of the axiomatic premises which underlie his paper, and emphasises the fact that he in no way endeavoured to prove the falsity of the atomic hypothesis, as he attempts to establish nothing contradictory to this hypothesis. What he does seek to show, however, is that the atomic hypothesis is not necessary to explain the laws of fixed and multiple proportions, and he states that he hopes to further show there is no necessity for its acceptance for the explanation of any of the known chemical facts. L. M. J.

Lecture Experiment with Liquid Carbonic Anhydride. By CARL BARUS (*Amer. J. Sci.*, [iv], **32**, 1—4).—The passage of liquid carbonic anhydride through the critical temperature is best shown by using sunlight and heating the tube containing the liquid carbonic anhydride in an air bath. The projected image of the whole tube is then clear, and the demarcation between liquid and vapour is unmistakable even at a distance. Moreover, the tube acts like a cylindrical lens, a sharp, silvery focal line being obtained both for the liquid and gaseous part. The two focal lines, however, are not coincident, and hence the projecting lens must be moved backwards and forwards to obtain sharp images of the linear foci corresponding to the vapour or the liquid respectively. This displacement of the projecting lens is considerable, being from 5—6 cm. with the usual tube, and the extreme

positions of the lens remain practically unchanged with temperature, whereas it would naturally be expected that the highly compressed gas and the liquid so near the point of continuously merging into gas would show similar refracting properties; in other words, it was thought that two linear foci would be found, one corresponding with the compressed gas, and the other with the liquid, at a distance apart which would gradually vanish as the critical temperature is approached. The author believes that there is no real continuity between CO_2 gas and CO_2 liquid at the critical temperature; but there is continuity between the liquid and a gas (C_3O_6) which preserves the same molecule, the same molecular structure as the liquid from which it issues. Doubtless at still higher temperatures the gas with the liquid molecule will break up into the true gas with the gaseous molecule, and the fact should be indicated by the sliding lens method mentioned above.

E. C. R.

Apparatus for Simultaneously Heating and Shaking Sealed Tubes. By EMIL FISCHER (*Ber.*, 1897, **30**, 1485—1487).—The author describes an apparatus for keeping sealed tubes in motion whilst they are being heated. This combination of heating and shaking has been found most useful in synthetical researches in the uric acid group. The apparatus consists of a rectangular copper vessel 60 cm. long × 27 broad × 43 high, closed by a lid having two perforations, one for a thermometer, and the other for the gas-regulator. The vessel, which is three parts filled with oil or other suitable liquid, is placed on an iron stand, and heated from below. Arms are attached to the sides of the copper vessel, and on these the mechanical contrivance for the shaking rests. The arrangement is such that this part of the apparatus, together with the sealed tubes, can be removed from the vessel even during the heating. The shaking must not be too rapid, not more than 10—15 oscillations per minute. The tubes should not be more than three-quarters full, and if there is no probability of their exploding, they are simply fixed into the frame between pieces of cork by means of screws. If there is any chance of an explosion, the tubes must be carefully packed in closed iron tubes by means of cotton wool, or asbestos and the capillary point must also be protected by means of a cork.

J. J. S.

Inorganic Chemistry.

Function of Peroxides in Phenomena of Slow Oxidation. By A. Bach (*Compt. rend.*, 1897, **124**, 951—954).—The author has made experiments with a view to ascertain whether slow oxidation is always accompanied by the formation of peroxides. The reagents used for the detection of the peroxides were titanic sulphate solution (1 gram of titanic acid dissolved in 20 c.c. of sulphuric acid and diluted to 100 c.c.), hypovanadous sulphate (1 gram of vanadic acid dissolved in 20 c.c. of hot sulphuric acid and diluted to 100 c.c.) and

the potassium dichromate, oxalic acid, and aniline method previously described (Abstr., 1895, ii, 239). It was found that peroxides are formed by the slow oxidation by air in the light or in the dark of nascent hydrogen (palladium), phosphorus, sodium, potassium, zinc, iron, lead, methylic, ethylic, and isopropylic alcohols, glycerol, formaldehyde, acetaldehyde, benzaldehyde, glucose, acetic, oxalic, and tartaric acids, ethylic ether, acetic anhydride, phenol, resorcinol, catechol, tannin, pyrogallol, dimethylaniline, diethylaniline, phenylhydrazine, formamide, acetamide, terebenthene, benzene, petroleum, quinine sulphate, morphine acetate, brucine, strychnine.

It would seem that all these compounds belonging to very varied groups are capable of forming peroxides during their slow oxidation. The oxidation involves the splitting up of the oxygen molecule $O\colon O$ and it may be taken that less energy is required to split it up into $\cdot O \cdot O \cdot$ than into $\cdot O \cdot$ and $\cdot O \cdot$. Consequently, in the earlier stages of the reaction, the substances combine with the grouping $\cdot O \cdot O \cdot$ and form peroxides. In some cases, tetroxides may be formed at the same time.

Peroxides may also be formed in cases of energetic oxidation. If a flame of hydrogen or carbonic oxide is directed on the surface of water, the latter afterwards gives the reactions of peroxides. In the case of carbonic oxide, percarbonic acid is produced.

When the peroxides have been formed, they help to continue and accelerate the oxidation. If air, for example, is passed through a solution of indigo mixed with terebenthene or benzaldehyde, the indigo is rapidly oxidised to isatin. Nascent hydrogen liberated from palladium produces a similar effect when oxidised by air, and in this case the indigo is completely oxidised when the quantity of active oxygen in the liquid is considerably less than that in the hydrogen peroxide that suffices to oxidise the indigo under ordinary conditions. The author considers that this result shows (1) that Hoppe-Seyler's view that the nascent hydrogen splits up the ordinary oxygen into one atom, with which it combines, and another which is set free and is capable of producing energetic oxidations, is not tenable; and (2) that the intermediate product is probably, not hydrogen peroxide, but hydrogen tetroxide.

In the blood, the readily oxidisable substances first form peroxides. and these oxidise the less readily oxidisable substances, in the same way as the peroxide formed by the terebenthene oxidises the indigo. The so-called oxidising ferments in the blood are simply readily oxidisable substances with a special aptitude for forming peroxides.

C. H. B.

The so-called Rendering Active ("Activirung") of Oxygen and the Formation of Peroxides. By CARL ENGLER and W. WILD (*Ber.*, 1897, **30**, 1669—1681. Compare Abstr., 1896, ii, 558 and 574, and preceding abstract).—When a substance is oxidised by atmospheric oxygen in presence of a compound capable, under other circumstances, of resisting its influence, it sometimes happens that the latter is also oxidised. Attempts have been made to explain the cause of this phenomenon (*Activirung*), Schönbein regarding it as dependent on preliminary conversion of oxygen into ozone and antozone, and a similar explanation having been put forward by Brodie and by Clausius, whilst

according to the view of Hoppe-Seyler and of Baumann, nascent hydrogen appropriates one atom of the oxygen molecule, and allows the remaining one to oxidise surrounding matter. M. Traube, on the other hand, ascribes the phenomenon to the resolution of water into hydroxyl and oxygen, the latter giving rise to hydrogen peroxide (Abstr., 1893, ii, 412).

It is the authors' opinion that molecules of oxygen, and not atoms, are involved in the action, which they regard as arising from preliminary formation of the peroxides, R_2O_2 and RO_2, these compounds then acting as oxidising agents. Oxygen behaving in the above-mentioned manner is, therefore, not at first atomic, but chemically combined and easily liberated. The experiments which have led to this generalisation are described in the paper. M. O. F.

Existence of Selenium Monoxide. By A. W. Peirce (*Amer. J. Sci.*, 1896, [iv], **2**, 163—167).—The odour of decayed cabbage which is noticed when selenium is burned in air was attributed by Berzelius to the formation of a gaseous selenium monoxide. Sacc (*Ann. Chim. Phys.*, 1847, [iii], **21**, 119), was unable to obtain any evidence of the formation of selenium monoxide and referred the peculiar smell mentioned above to the formation of a small quantity of selenium hydride which would be produced when selenium is heated in the presence of moisture, and a small trace of moisture is sufficient to produce the odour.

Chabrié (*ibid.*, 1890, [vi], **20**, 273) has stated that selenium, when heated at 180° in the air, undergoes an increase in weight very nearly corresponding with that required for the formation of the monoxide. The selenium which he employed was obtained from certain organic compounds by reducing the products of oxidation with sodium sulphite and hydrochloric acid. The author has heated selenium, prepared from the dioxide and dried to a constant weight at 100°, for various lengths of time at 110° to 180°, and in every experiment a loss of weight was observed. This loss is due to the volatilisation of the selenium as such. A mixture of selenium and selenium dioxide was heated in a tube at a pressure of 4 mm. at 180—200°; the contents of the tube were vaporised and maintained in that condition for 7 hours, but no gaseous products were found, and the contents of the tube possessed no odour. E. C. R.

Atomic Weights of Nitrogen and Arsenic. By Joseph Gillingham Hibbs (*J. Amer. Chem. Soc.*, 1896, **18**, 1044—1050).—The method consists in determining the amount of metallic chloride obtained from sodium or potassium nitrate or arsenate when they are heated in a current of hydrogen chloride.

The mean of five experiments gave the atomic weight of nitrogen by the action of hydrogen chloride on potassium nitrate $N = 14{\cdot}0118 \pm 0{\cdot}000472$. With sodium nitrate, the mean of five experiments was $N = 14{\cdot}0116 \pm 0{\cdot}000741$. If these results are compared with those obtained by Penny and by Stas by treatment of potassium chloride with nitric acid, and the treatment of potassium nitrate with hydrochloric acid and also their results for the sodium salt, a close comparison can be made. Penny obtained for potassium nitrate $N = 13{\cdot}9774$, for sodium

nitrate N = 13·9906. The mean of all the author's results gives the atomic weight of nitrogen as 14·0003; when O = 16, K = 39·11, Cl = 35·45, Na = 23·05.

The determination of the atomic weight of arsenic is effected in a similar way by the action of hydrogen chloride on sodium pyroarsenate The mean of ten determinations gave As = 74·9158 ± 0·00222.

E. C. R.

Combustion of Nitrogen. By OTTO BLEIER (*Ber.*, 1897, **30**, 1269. Compare this vol., ii, 280, and Lord Rayleigh, Trans., 1897, 181).—The nitrogen is mixed with the requisite quantity of oxygen either in an enamelled autoclave or in a thick-walled explosion pipette in which dilute alkali is placed. A considerable amount of electrolytic gas is added and then exploded, the oxides of nitrogen removed by shaking with the alkali and a further quantity of electrolytic hydrogen and oxygen added and again exploded. To remove all the nitrogen, it is necessary to repeat the operation several times.

J. J. S.

Nitrogen Chloride. By W. HENTSCHEL (*Ber.*, 1897, **30**, 1434—1437).—Nitrogen chloride dissolved in various solvents can be preserved for some time in the dark, but rapidly decomposes on exposure to a bright light. The solution in benzene is obtained by adding ammonium chloride to a 5 per cent. solution of soda which has been treated with chlorine, and agitating with benzene. About seven-eighths of the active chlorine of the aqueous solution is converted into nitrogen chloride. The solution is a clear, strongly refractive, sulphur-yellow liquid, and possesses the characteristic repulsive odour of nitrogen chloride. When exposed to sunlight, it decomposes, nitrogen being evolved and benzene hexachloride produced. The solution in carbon bisulphide yields sulphur chloride, whilst that in carbon tetrachloride simply gives nitrogen and chlorine. On the other hand, solutions in chloroform and in ether do not yield nitrogen but ammonia, ammonium chloride separating out, and hydrogen chloride and chlorine being evolved. The chloroform also yields a trace of hexachlorethane, and the ether a liquid which boils at 80—150°, contains chlorine and reduces silver chloride.

A. H.

Molecular Weight of Arsenamphide Compounds. By EMERICH SZARVASY and CARL MESSINGER (*Ber.*, 1897, **30**, 1343—1347).—Earlier vapour density determinations have shown that $2As_2O_5$ is already dissociated into As_4O_6 and $2O_2$ at a dull red-heat, whilst As_4O_6 is stable at 1560°; and that As_2S_5 is dissociated at about 500° into As_2S_3 and S_2, whilst As_2S_3 is not dissociated at 700°, but begins to be so at 1000°. It has now been found that As_2S_2 (normal vapour density 7·40) has a density varying from 19·16 at 450° to 6·95 at 1200°; As_4S_3 (normal 13·69) gives 8·20 at 792°, 6·59 at about 1000°. As_2Se_5 (normal 18·84) gives 9·59 at about 800°; 7·41 at about 900°; As_2Se_2 (normal 10·65) gives 10·54 at 900°, and 6·22 at 1050—1100°; As_2Se (normal 7·92) gives numbers varying from 15·48 at 617° to 7·55 at 1159°. It will be noticed that the stability decreases in the series As_4O_6, As_4S_4, As_4Se_2; further, that the oxygen compounds are the most stable, the selenium ones the least so.

C. F. B.

Action of Acid Vapours on Metallic Sulphides. By JEROME KELLEY and EDGAR FRANCIS SMITH (*J. Amer. Chem. Soc.*, **18**, 1096—1098).—Arsenic trisulphide is completely volatilised in a current of hydrogen bromide; the action commences in the cold with the production of a liquid which passes out of the containing vessel on the application of a very gentle heat. Antimony trisulphide and stannic sulphide are completely volatilised in a current of hydrogen bromide or hydrogen chloride. Stannous sulphide, by the continued action of the gas in the cold, is completely converted into chloride without any volatilisation. It is, however, impossible to separate stannous and stannic sulphides by this method, as heat is necessary to drive out the stannic salt, and this causes a partial volatilisation of the stannous chloride. E. C. R.

Arsenic Monoselenide and the Vapour Density of Selenium. By EMERICH SZARVASY (*Ber.*, 1897, **30**, 1244—1248).—The author has determined the vapour density of selenium, by V. Meyer's method, at temperatures between 774° and 1165°. At 774°, the density is 7·03, and then gradually diminishes until it becomes constant at about 900—950°, when it agrees with the formula Se_2 (= 5·466).

Arsenic monoselenide, As_2Se, was prepared by melting the two constituents in the requisite proportions, or with a very slight excess of arsenic, the operation being carried out in a sealed tube filled with nitrogen. The combination took place at about 600°, and the product, which consisted mainly of the monoselenide, was sublimed under pressure in an atmosphere of nitrogen. It forms black, metallic-looking crystals, giving a black streak. It is insoluble in the usual organic and inorganic solvents; concentrated hydrochloric and sulphuric acids act on it but slowly, boiling alkali hydroxides, however, decompose it in much the same manner as they do the lower sulphides of arsenic. The vapour density at 617° corresponds with the formula As_4Se_2, but at 1002° it corresponds with the formula As_2Se, and above this temperature dissociation into its elements occurs. This is the most stable of the arsenic-selenium compounds. J. J. S.

The Amount of Carbonic Anhydride in the Atmosphere. By W. CARLETON WILLIAMS (*Ber.*, 1897, **30**, 1450—1456).—The estimations were made by a modification of Pettenkofer's method, the baryta water being filtered from the precipitated carbonate in an atmosphere free from carbonic anhydride, and the titration then effected with hydrochloric or nitric acid. Allowance was also made by means of blank experiments for the action of baryta on the glass.

The results show that the air of Sheffield (centre of the town) contains on the average 3·9 parts of carbonic anhydride in 10,000, the maximum observed in 22 estimations being 6·22 and the minimum 2·80. At a distance of 1·5 miles west of this point, the average of 142 experiments was 3·27 parts, the maximum being 5·14 and the minimum 2·16. Snow and fog clearly increase the amount present, whilst rain has no influence. Very high and very low atmospheric pressure are accompanied by an increase in the amount of carbonic anhydride, whilst the amount decreases as the temperature rises.

A. H.

Constitution of the Metallic Carbonyls. By ANTONIO J. FERREIRA DA SILVA (*Bull. Soc. Chim.*, 1897, [iii], **15**, 835—838).—The author discusses the results which have already been obtained by others. He is of the opinion that in the carbonyl derivatives of iron, nickel, and platinum, the carbon atoms do not form a chain, but are connected directly to the metallic atom. M. W. T.

Influence of Pressure on the Solubility of Quartz in Water. By GIORGIO SPEZIA (*Zeits. Kryst. Min.*, 1897, **28**, 200—201; from *Atti Accad. Sci. Torino*, 1896, **31**, 246—250. Compare Abstr., 1896, ii, 257).—Pfaff found at a temperature of 18°, and under a pressure of 290 atmospheres, one part of quartz to be dissolved in 4700 parts of water; the present author points out that, owing to experimental errors, this solubility is too high. He found that plates of quartz kept for several months in water at 27° under pressures of 1750 and 1850 atmospheres did not diminish in weight, and showed no etch figures. Pressure alone has therefore little influence on the solubility of quartz. L. J. S.

Constitution of Metallic Alloys. By GEORGES CHARPY (*Compt. rend.*, 1897, **124**, 957—959).—Micrographic examination shows that eutectic alloys are not definite compounds, but contain two constituents in juxtaposition in the form of extremely thin lamellæ, which are only distinguishable under high magnification. The thinness of the crystals explains the homogeneous appearance of the alloys, which often have a conchoidal fracture. It follows that eutectic alloys are analogous in constitution to the cryohydrates, and are to be regarded as mixtures of constant condensation, like mixtures of liquids which distil at a fixed temperature.

The constituent of steel, called *perlite* by Osmond, has a constitution similar to that of eutectic alloys, and this is another reason against Arnold's view that it is a definite iron carbide.

The same method of examination, however, also proves the existence of certain definite compounds. The compound $SnCu_3$ is readily recognisable in tin-copper alloys containing 5 per cent. of copper, and forms hard, white crystals, generally six-pointed stars similar to snow crystals, their proportion increasing with the percentage of copper, and ultimately constituting the whole mass when it has the exact composition $SnCu_3$. The compound $SbCu_2$ is likewise readily recognisable in copper antimony alloys. The method indicates the existence of several definite compounds that have not yet been isolated, for example, a compound of tin and antimony containing 50 per cent. of the former and isomorphous with the latter; a compound of antimony and silver containing 20 per cent. of the former and isomorphous with the latter; a compound of tin and silver containing 30 per cent. of the former and isomorphous with the latter.

In the microscopic examination of an alloy, colour, hardness, and behaviour towards various reagents are often of more value than the form of the constituents, and they often, in fact, enable a proximate analysis to be made.

There are two normal types of binary alloys. One shows crystals of a definite constituent, which may be either a single metal or a definite

compound of two, embedded in a second constituent which, as a rule, is an eutectic mixture with the structure already described. The second type contains isomorphous mixtures formed throughout its mass of a single kind of crystal, the composition and properties usually varying continuously from the exterior to the interior of each crystal. This type is somewhat common, for whilst there are a few metals that form isomorphous mixtures, there are several instances of definite compounds of two metals which are isomorphous with one of their constituents. C. H. B.

Action of Potassium Permanganate on Cupric Bromide. By HENRI BAUBIGNY and PAUL RIVALS (*Compt. rend.*, 1897, **124**, 954—956).—When the solution in which cupric bromide has been decomposed by potassium permanganate is evaporated to dryness and treated with water, an insoluble residue is left which, after being dried at 120—125°, contains no alkali, but cupric oxide, manganese peroxide, sulphuric anhydride, and water, in the proportions $21CuO,8MnO_2,5SO_3,18H_2O$. The sulphuric acid is wholly in combination with the copper in the form of the basic salt, $CuSO_4,3Cu(OH)_2$, whilst the remaining elements are in the proportions required to form the compound, $Cu(H_3Mn_4O_{10})_2$, corresponding with the potassium salt which is always formed when potassium permanganate oxidises carbon compounds in neutral solution. It follows that the action of the permanganate on the cupric bromide is strictly analogous to its action on carbon compounds. The complete equation is $24KBr + 8KMnO_4 + 21CuSO_4 + 18H_2O = 12Br_2 + Cu(H_3Mn_4O_{10})_2 + 5[CuSO_4,3Cu(OH)_2] + 16K_2SO_4$. The presence of an excess of cupric sulphate is necessary in order to prevent formation of the oxybromide and also to compensate for the fact that part of the copper combines with the manganese oxide. Cupric chloride is as effective from this point of view as the sulphate. An excess of permanganate is also desirable in order to ensure complete and rapid decomposition. C. H. B.

Preparation of Aluminium Chloride. By RICHARD ESCALES (*Ber.*, 1897, **30**, 1314—1317).—The author finds that in Stockhausen and Gattermann's method of preparing aluminium chloride, it is unnecessary to heat the aluminium throughout the reaction, since the action, when once started, is carried on by the heat arising from the combination. He therefore prepares this compound in the following way. A stream of dry hydrogen chloride is passed into a tubulated bell-jar in which a large glass dish is placed, having in the centre a glass tripod supporting a plate of asbestos, on the asbestos is placed about 20 grams of aluminium filings, the hydrogen chloride is then passed in, and the action started by pouring in a small quantity of strongly heated aluminium through the opening in the bell-jar on to the asbestos plate; the action then continues until all the aluminium has been converted into chloride. It can be collected from the sides of the jar and from the glass dish, the yield being about 70—75 per cent. J. F. T.

Saturation of Iron by Carbon. By HANNS VON JÜPTNER (*Chem. Centr.*, 1896, ii, 653; from *Österr. Zeit. Berg-Hütt.*, **44**, 447—449).

—Whilst the presence of manganese and chromium in iron increases its capacity of taking up carbon, on the other hand, sulphur, silicon, most metalloids, as well as phosphorus, arsenic, antimony, tin and aluminium, have an opposite effect. For pure iron, Percy gives the maximum content of iron = 4·63 per cent. corresponding with $Fe_{4\cdot4}C$. From Ledebur's data for the maximum content of carbon in iron containing various amounts of manganese and chromium, the author finds the carbon saturation power of the latter by calculation to be respectively 7·75 per cent., corresponding with $Mn_{2\cdot3}C$ and 11·6 per cent. corresponding with Cr_2C. These values appear to be quite independent of the iron present. The diminution in the carbon saturation power of iron caused by silicon, &c., depends probably on the substitution of the one element for the other in the ratio of their atomic weights although this power of taking up carbon is never entirely destroyed by these elements. In a carbon saturated iron containing 83·53 per cent. of iron, 5·17 manganese, 10·19 phosphorus, and 1·11 carbon, the theoretical percentage of carbon corresponding with the iron and manganese present is 4·47 per cent. Hence the presence of 10·19 per cent. of phosphorus has diminished the saturation power by 3·36 per cent., which corresponds with P : 0·85C. The author regards E. Donath's hypothesis of the presence of closed chain compounds in iron containing carbon as the best explanation, and suggests that silicon, sulphur, phosphorus, &c., may also be contained in such compounds.

E. W. W.

Ferric Hydroxide in Precipitation. By VERNON J. HALL (*Amer. Chem. J.*, 1897, **19**, 512—525).—The author has studied the precipitation of ferric hydroxide with reference to its effect in carrying down potassium sulphate. The results of the work show that the equation $Fe_2Cl_6 + 6KOH + 4K_2SO_4 = Fe_2(OH)_6 + 6KCl + 4K_2SO_4$, which has been suggested, does not completely represent the reaction. As was the case with aluminium, the results show the mechanical inclusion theory to be inadequate, and point towards a phenomenon of a strictly chemical nature, such as the formation of a salt of ferric hydroxide and potassium, analogous to potassium aluminate.

A. W. C.

Tungsten Hexabromide. By HERBERT A. SCHAFFER and EDGAR F. SMITH (*J. Amer. Chem. Soc.*, **18**, 1098—1100).—*Tungsten hexabromide* is obtained by gently heating tungsten with bromine in an atmosphere of nitrogen. It forms bluish-black, crystalline masses, melts readily, and when carefully resublimed forms blue-black needles. It is decomposed when heated at a high temperature, fumes when brought into contact with the air, is decomposed by water with the formation of a royal-blue oxide, and dissolves in aqueous ammonia to a colourless solution.

E. C. R.

Action of Ferric Chloride on Metallic Gold. By PARKER C. MCILHINEY (*Amer. J. Sci.*, [iv], **2**, 293—294).—Hydrochloric acid in the presence of air is without action on metallic gold, but if a small quantity of ferric chloride is present (about $\frac{1}{50}$th of the weight of the gold) gold is dissolved. The solution is due to the action of the oxygen, which reacts with the hydrochloric acid and the gold to produce water

and gold chloride, provided that ferric chloride is present to act as a carrier of chlorine.

A mixture of hydrochloric acid and ferric chloride free from oxygen and protected from the air does not dissolve the slightest trace of gold. E. C. R.

Mineralogical Chemistry.

Artificial Cotunnite. By F. STÖBER (*Zeit. Kryst. Min.*, 1897, **28**, 108—109; from *Bull. Acad. Belg.*, 1895, **30**, 345).—Very good orthorhombic crystals of cotunnite ($PbCl_2$) are deposited from a solution of lead chloride in concentrated hydrochloric acid, the crystals being grown on a glass float in the liquid. The results of detailed crystallographic and optical measurements are given. $a:b:c = 0·5013:1:0·8423$. Twinning on (021) is frequent. There is a fairly perfect cleavage parallel to (010). When a hot, aqueous solution of lead chloride is slowly cooled, tabular crystals are obtained, but when quickly cooled, acicular crystals result. Becquerel's "cubic" crystals of lead chloride are probably only cotunnite with the forms {100}, {010} and {001}.

L. J. S.

Altaite from Burma. By HENRY LOUIS (*Min. Mag.*, 1897, **11**, 215—216).—Altaite occurs in minute, crystalline grains in the gold mines at Choukpazat, Wuntho, Upper Burma, where it is associated with quartz, calcite, pyrites, mispickel and native gold. The colour is tin-white, with a somewhat yellowish tinge, and a high metallic lustre. There is a perfect cubic cleavage. The mineral appears to be brittle (altaite is usually stated to be sectile); H = 2—3. Analysis gave the results under I, and after deducting impurities, II; this agrees very closely with the formula PbTe.

	Te.	Pb.	Fe.	Ag.	$CaCO_3$.	SiO_2.	Total.
I.	34·2	57·4	0·2	trace	3·8	2·1	97·7
II.	37·4	62·6	—	—	—	—	100·00

The altaite occurs in the richer auriferous portions of the veins, and films of gold are sometimes deposited between the cleavage planes of the altaite.

L. J. S.

Nemalite from Afghánistán. By FREDERICK R. MALLET (*Min. Mag.*, 1897, **11**, 211—214).—Specimens of nemalite from Afghánistán consist of a mass of straight, very fine, highly flexible and elastic, easily separable fibres 8 inches long, which seem clearly to have formed part of a vein in serpentine. The colour is sea-green with a silky lustre, and the fibres are inclined at an angle of about 20° to the walls of the vein. The fresh central portion gave on analysis:

MgO.	FeO.	MnO.	CaO.	H_2O.	SiO_2.	Total.	Sp. gr.
62·00	7·87	trace	trace	29·55	0·38	99·80	2·454

When the mineral is decomposed by hydrochloric acid, the silica is

left in a fibrous form, as is the case with chrysotile; the 0·38 per cent. of silica is therefore considered to represent 0·88 per cent. of admixed chrysotile, which may be original or secondary. The material forming the outer portions of the veins is somewhat altered, being reddish or white and opaque. It contains 0·26 per cent. of silica with some carbonic anhydride and ferric oxide, and passes into scaly hydromagnesite enclosing magnetite.

L. J. S.

[Brown Spar from Goldkronach, Bavaria.] By FRIDOLIN VON SANDBERGER (*Ber. Akad. München*, 1894, **24**, 244).—In a paper (pp. 231—248) describing the ore deposits at Goldkronach near Berneck in the Fichtelgebirge, and all the minerals found there, the following analysis by Hilger is given of "brown spar" [ankerite] which is of a pale, flesh-red colour on the exterior, but is white on the cleavage surfaces. Sp. gr. 3·05.

$FeCO_3$.	$MnCO_3$.	$CaCO_3$.	$MgCO_3$.	Total.
18·470	3·063	56·066	21·997	99·596

L. J. S.

A Neutral "Phosphoreisensinter." By O. RAU (*Zeit. Kryst. Min.*, 1895, **24**, 613—614).—In the coal mine Königin Luise, Pachtfeld, near Zabrze, in Upper Silesia, not far from the clay slate, are cavities filled with a reddish-brown to light-yellow, glassy, transparent mineral; it is very brittle, and has a conchoidal fracture. It has no action on polarised light. Sp. gr. 2·18; H = 3—3·5. In the air, it lost 0·46 per cent. of moisture in 7 days; over sulpuric acid for 10 days, there was a loss of 12·11 per cent. At 100°, a loss of 17·69, and at 150° of 22·03 per cent. without attaining a constant weight. The mean amount of the total water was 32·01 per cent. Pieces which were clouded by the presence of numerous fractures gave slightly different amounts of water. Analyses of the transparent material are given under I and II.

	Fe_2O_3.	P_2O_5.	SO_3.	H_2O.
I.	32·05	20·00	14·38	33·02
II.	33·12	20·12	14·33	33·62
III.	0·80	0·00	10·72	—

Hot water extracted from the powdered mineral the amounts given under III. The formula is given as $5(Fe_2O_3,P_2O_5) + 2(Fe_2O_3,3SO_3) + 60H_2O$. This is near to diadochite, which, however, has a slight excess of iron beyond that required by the above neutral formula.

L. J. S.

Derbylite from Tripuhy, Brazil. By EUGEN HUSSAK and GEORGE T. PRIOR (*Min. Mag.*, 1897, **11**, 176—179).—The new antimonotitanate of iron (Abstr., 1895, ii, 508), which is found with lewisite in the cinnabar-bearing gravels of Tripuhy, Minas Geraes, has now been obtained in sufficient quantity for detailed determination, and it is here called derbylite.

The small orthorhombic crystals are frequently twinned on (011), giving rise to staurolite-like forms. $a:b:c = 0·96612:1:0·55025$. The mineral is pitch-black in colour, with a resinous lustre; it is trans-

lucent in very thin splinters only, and is biaxial. There is a conchoidal fracture parallel to (001). Sp. gr. 4·530; hardness about 5, but very brittle. It is insoluble in acids, but is decomposed by fusion with potassium hydrogen sulphate. The more complete of the two analyses by G. T. Prior is given below.

Sb_2O_5.	TiO_2.	SiO_2.	Al_2O_3.	FeO.	CaO.	Na_2O.	K_2O.	Loss on ignition.	Total.
24·19	34·56	3·50	3·17	32·10	0·32	0·76	0·28	0·50	99·38.

Neglecting the silica, alumina and alkalis as due to the presence of muscovite, the formula is given as $FeO,Sb_2O_5 + 5(FeO,TiO_2)$. Details are given of the methods of analysis; the mineral was first decomposed by heating in a current of hydrogen. Lewisite and derbylite have recently been found in the cinnabar-bearing gravels enclosed in fragments of muscovite-schist. L. J. S.

Composition of Zirkelite. By George T. Prior (*Min. Mag.*, 1897, **11**, 180—183).—The previous analysis (Abstr., 1895, ii, 508) of this new isometric mineral from Jacupiranga, Brazil, was unsatisfactory, owing to the difficulties of separation with the small amount of material then available. A new analysis on more material (0·4716 gram) gave:

ZrO_2.	TiO_2.	ThO_2.	Ce_2O_3.	Y_2O_3?.	UO_2.	FeO.	CaO.	MgO.	Loss on ignition.	Total.
52·89	14·95	7·31	2·52	0·21	1·40	7·72	10·79	0·22	1·02	99·03.

The formula is given as $RO,2(Zr,Ti,Th)O_2$. Sp. gr. 4·741.

The mineral was decomposed by fuming hydrofluoric acid, and the titanium estimated by Weller's colorimetric method. Full details of the methods of analysis are given. L. J. S.

Celsian, a Barium Felspar corresponding with Anorthite. By S. A. Hjalmar Sjögren (*Geol. Fören. i Stockholm Förh.*, 1895, **17**, 578—582).—Barium felspar from Jakobsberg, Sweden, has been previously described by Igelström under the name of hyalophane, but no optical determinations were made. The mineral now described from this locality occurs in the massive state with schefferite and manganophyllite; it is clear and colourless, and shows the ordinary felspar cleavages, $c(001)$, $b(010)$, together with $m(110)$ and $M(1\bar{1}0)$ less distinct; the cleavage angle cb is about $89\frac{1}{2}°$. On $c(001)$ the angle of optical extinction is 3° 10′, and on $b(010)$ 26° 45′ referred to the edge cb; an acute bisectrix emerges obliquely through c; these characters show the mineral to be anorthic. Sp. gr. 3·37; H over 6. It is easily and almost completely decomposed by hydrochloric acid. Analysis by R. Mauzelius on material dried at 110° gave:

SiO_2.	Fe_2O_3.	Al_2O_3.	BaO.	CaO.	MgO.	K_2O.	Na_2O.	H_2O.	F.	Total less O for F.
32·43	0·12	26·55	39·72	0·23	0·11	0·22	0·16	0·64	0·64	100·55.

At 370°, 0·44 per cent. of the water is lost. This agrees closely with $BaAl_2Si_2O_8$, and it is thus an almost pure barium felspar analogous to anorthite. L. J. S.

Phenakite from Silesia. By Carl Hintze (*Zeit. Kryst. Min.*, 1897, **28**, 174—176).—The occurrence of crystallised phenakite in

cavities of the Striegau granite is recorded. Frenzel found BeO, 45·46; SiO_2, 54·54 per cent., and a trace of iron. Sp. gr. 3·02.

L. J. S.

Beryl containing Cæsium from Galicia. By FEDERICO CHAVES Y PÉREZ DEL PULGAR and FEDERICO RELIMPIO Y ORTEGA (*Anal. Soc. Españ. Hist. Nat.*, 1895, **24**, Actas 7).—Cæsium has been detected by a microchemical reaction (with stannic chloride) in a clear crystal of light green beryl from Galicia, Spain. L. J. S.

Gonnardite. By ALFRED LACROIX (*Bull. soc. fran. min.*, 1896, **19**, 426—429).—The doleritic basalts near Gignat, Puy-de-Dôme, which form the plateau of Chaux-de-Bergonne, contain numerous zeolites in their cavities; one of these, which has been described as mesolite by Gonnard (*Compt. rend.*, 1871, **73**, 1147), is shown by its optical characters to be a new species, to which the name gonnardite is here given. It is white and fibrous, and forms spherical concretions about the size of a pea. The acute positive bisectrix is parallel to the length of the fibres, this character distinguishing the mineral from mesolite and thomsonite. The optic axial angle is very small and is sometimes zero; the birefringence is weaker than that of mesolite and thomsonite. The crystalline system is possibly orthorhombic. The formula, $(Ca,Na_2)_2Al_2Si_5O_{15} + 5\frac{1}{2}H_2O$ with $CaO:Na_2O = 5:3$, deduced from Pisani's old analysis, is doubtful, since, under the microscopic, the mineral is seen to be intergrown with scolecite? and sometimes with thomsonite. Gonnard has given the sp. gr. as 2·246—2·357.

L. J. S.

Asbestos and Asbestiform Minerals. By GEORGE P. MERRILL (*Proc. U.S. National Museum*, 1896, **18**, (1895), 281—292).—It is shown that the name asbestos, as commercially used, includes at least four distinct minerals, which only have in common a fibrous structure and more or less fire- and acid-proof properties; they are (1) tremolite or asbestos proper, (2) serpentine (amianthus), (3) anthophyllite, and (4) crocidolite. The first two of these are, as a rule, easily distinguished, but tremolite and anthophyllite are easily confused, and can only be distinguished by optical and chemical means. Of the twenty-four analyses made by the author and R. L. Packard, twelve are of anthophyllite, seven of asbestiform tremolite, and two of uralitic augite. It is considered that the fibrous structure of these minerals has been produced by a process of shearing, the original minerals being amphiboles and probably sometimes pyroxenes. L. J. S.

Mica from Co. Dublin. By J. P. O'REILLY (*Min. Mag.*, 1897, **11**, 199—210).—The white mica of the Three Rock Mountain, Co. Dublin, often encloses, zonally arranged, black and brown specks which sometimes show hexagonal outlines, and may possibly be melaconite. The microscopic characters of blue and green spots are also described in detail. After the separation of the black particles, the white mica gave analysis I by Miss M. W. Robertson: at 100°, there is a loss of 0·2506, and between 100—240° of 0·1058 per cent. Hydrochloric acid dissolves out the colouring matter from the black particles, leaving a residue of white mica, the soluble portion consisting of 9·78—22·5

Cu_2O, and 25·35—45·14 Fe_2O_3 per cent. In a note by W. N. Hartley it is stated that there were no black specks, but only bright red spangles, in the material analysed, and that the copper was shown to be present as cuprous and not as cupric oxide.

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	Cu_2O.	CaO.	MgO.
I.	39·414	33·738	1·418	—	1·244	3·654	0·955	1·344
II.	42·99	34·44	—	2·69	0·06	0·10	0·54	0·77

	K_2O.	Na_2O.	Li_2O.	F.	Loss on ignition.	Total.
I.	9·430	2·675	0·642	trace	4·710	99·224
II.	13·29	trace	—	—	5·05	99·91

Analysis by C. Darling of a mica containing copper from Glencullen, Co. Wicklow, is given under II. L. J. S.

[Forsterite, Hornblende, Nontronite, Batavite, and Garnet from Bavaria.] By Ernst Weinschenk (*Zeit. Kryst. Min.*, 1897, **28**, 135—164).—Various minerals which occur in connection with the graphite deposits in the gneiss to the north of Passau are described; analyses are given of the following. Blue quartz occurs, with other minerals, embedded in the graphite itself; when treated with hydrofluoric acid, there was a residue of 0·056 per cent. which contained iron and manganese. In the associated metamorphic limestone are, amongst other minerals, colourless forsterite (anal. I) and crystals of hornblende ("pargasite," anal. II); in I is included a residue of 1·92 per cent. which was unattacked by hydrochloric acid. Nontronite occurs in the syenites as a decomposition product and as pseudomorphs after hornblende; after deducting hornblende, its composition is given under III, from which the formula is deduced as $H_4Fe_2Si_2O_9$. Owing to the hygroscopic nature of the material, the water given off at 110° varies from 5·00 to 10·62 per cent.; the remainder of the water, which is that shown in the analysis, is given off on ignition. The optical characters agree with monoclinic symmetry. *Batavite* is the name given to a white, scaly decomposition product which occurs with the nontronite and with kaolin. It closely resembles nacrite (kaolin) in appearance, but differs from it in giving a bulky precipitate of magnesia when decomposed by a solution of caustic soda. The mean of two analyses on material dried at 110° is given under IV, from this the formula is given as $2[Al(OH)_2]4(MgOH)Si_4O_{13}$. It appears to be somewhat related to the micas, and under the microscope sometimes shows hexagonal outlines.

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	MgO.	Na_2O.	H_2O.	Total.	Sp. gr.
I.	43·37	—	—	4·17	1·41	0·00	48·40	—	—	99·27	3·242
II.	46·38	15·33	0·00	1·51	—	13·14	20·24	1·78	1·21	99·59	3·048
III.	38·97	1·26	48·34	—	—	—	—	—	11·43	100·00	—
IV.	42·33	16·35	—	—	—	—	28·17	—	13·19	100·04	2·183
V.	48·58	17·52	4·74	0·00	trace	11·21	13·24	—	5·00	100·29	3·052
VI.	36·88	19·58	2·14	13·48	27·14	1·71	—	—	—	100·93	—
VII.	38·77	19·32	36·67		trace	4·17	—	—	—	98·93	—

A mineral from Bodenmais, which has been called anthrophyllite, is shown to be common hornblende (anal. V) with the formula $3R''_4Si_4O_{12} + 2R''_4R'''_4Si_2O_{12}$. Spessartite, which occurs as isotropic crystals in pegmatite near Aschaffenburg (compare Abstr., 1896, ii,

310, 312), gave analysis VI, by E. Schröder. Almandine from granite near Aschaffenburg gave VII, by O. Wehr. L. J. S.

Tourmaline from Caprera, Sardinia. By Domenico Lovisato (*Zeit. Kryst. Min.*, 1897, **28**, 183; from *Atti R. Accad. Lincei*, Rend. 1895, [v], **4**, (1), 84—87).—Tourmaline, which has previously been known from only one locality in Sardinia, has been found by the author at several places in the orbicular granite and in the adjacent schists and gneisses. On the island of Caprera, it occurs as black crystals of sp. gr. 2·95—3·05; analysis by M. Fasolo, on material containing some quartz, gave

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	Mn_2O_3.	MgO.	CaO.	Na_2O.	B_2O_3.	F.	Total.
40·09	36·41	8·16	1·56	0·79	2·40	0·28	1·25	7·14	1·93	100·01

At a dull red heat there is a loss of 2·15 per cent. Potassium was detected spectroscopically. L. J. S.

[Hedenbergite and Epidote] from Sardinia. By Domenico Lovisato (*Zeit. Kryst. Min.*, 1897, **28**, 184—185; from *Atti R. Accad. Lincei*, Rend. 1895, [v], **4**, (1), 111—116).—In the schists of Su Porru, between Fonni and Cereboi, is a mineral having the appearance of epidote but which is shown by the analysis (I) of Fasolo to be hedenbergite with the formula $2MnO,3FeO,5CaO,10SiO_2$. Before the blowpipe it fuses to a black, magnetic mass. It is decomposed by warm hydrochloric acid, giving a yellow solution, gelatinous silica, and an insoluble residue.

In the same rock are greenish-yellow, translucent needles, which are shown by Fasolo's analysis (II) to have the formula

$$MnO,8CaO,Fe_2O_3,6Al_2O_3,16SiO_2,$$

and so to be epidote poor in iron. In the older trachyte are spheroids which in the interior consist of green, translucent epidote; analysis by Frasolo gave the results under III; the loss of 2·83 per cent. takes place between 210° and red heat.

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	MgO.	Na_2O.	TiO_2.	H_2O.	Total.	Sp. gr.
I.	48·48	—	—	17·46	10·92	22·62	0·32	—	—	0·32	100·12	3·446
II.	41·97	28·60	5·48	—	3·10	19·55	trace	—	—	0·71	99·41	3·126
III.	42·25	20·35	11·87	0·31	—	18·65	2·13	1·47	0·02	2·83	99·88	3·04–3·16

Epidote is found in all the crystalline rocks of Sardinia.

L. J. S.

Simple Massive Minerals. By John W. Judd (*Min. Mag.*, 1895, **11**, 56—63).—Several simple crystalline rocks, each composed essentially of a single mineral, are described; these include a purple corundum rock from Pipra in South Rewah, India, and a grey corundum rock from the Mysore State; a fibrolite rock and a tourmaline rock from India; a green garnet rock and a picotite rock, which occur as dykes in the serpentine at Bingera, New South Wales. The black tourmaline or schorl rock is dull and fibrous and in part velvety, and under the microscope is seen to consist of small, acicular crystals of tourmaline. An analysis gave:

SiO_2.	Al_2O_3.	FeO.	CaO.	MgO.	Na_2O.	Li_2O.	H_2O.	B_2O_3.	Total.
35·94	31·22	9·23	1·66	5·53	3·96	trace	3·55	9·08	100·17

Fluorine, phosphoric acid, manganese, potassium and titanium are absent. Sp. gr. 3·02—3·11. L. J. S.

Andradite from Ontario. By BERNARD J. HARRINGTON (*Canadian Record Sci.*, 1896, **6**, 479—481).—The magnetite of the "Paxton Iron Mine," Lutterworth township, Ontario, is associated with garnet, pyroxene, hornblende, &c. The garnet is black, and is mostly massive, but also in crystals. Sp. gr. 3·813. Analysis gave:

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	MgO.	Loss on ignition.	Total.
35·68	5·88	23·70	3·65	0·81	29·64	0·35	0·28	99·99

This reduces to the garnet formula. Titanium is absent. L. J. S.

Synthesis of Iron Silicates. By FEDERICO CHAVES Y PÉREZ DEL PULGAR (*Anal. Soc. Españ. Hist. Nat.*, 1896, **24**, Actas 157—158).—The following experiment was made in connection with the study of glauconite. A syrupy solution of sodium silicate and small fragments of ferrous sulphate were kept in an open vessel for 20 months, water being added as evaporation took place. Besides sodium sulphate, white grains and a greenish-grey, crystalline powder were formed; these were insoluble in water, but decomposed by nitric acid with separation of pulverulent silica, the solution containing iron, sodium, and potassium (the potassium was introduced as an impurity in the sodium silicate). L. J. S.

Analysis of a Barytes Rock. By FEDERICO CHAVES Y PÉREZ DEL PULGAR (*Anal. Soc. Españ. Hist. Nat.*, 1895, **23**, Actas 260—261).—A grey, compact, granular barytes rock from Peñaflor, Seville, described by Calderón (*Anal. Soc. Españ. Hist. Nat.*, 1894, **23**, 20) gave on analysis:

$BaSO_4$.	Fe_2O_3.	H_2O (at 170°).	SiO_2, Ca, Alkalis.	Al, Mn, Co.
80·6505	16·7752	0·0320	not estimated.	traces.

Sp. gr. 4·02. Thin sections under the microscope show plates of barytes, with magnetite, and as accessories, calcite, leucoxene, garnet, chlorite and felspar. L. J. S.

Gypsum Rocks from Kansas. By EDGAR H. S. BAILEY and W. M. WHITTEN (*Kansas Univ. Quart.*, 1897, **6**, A, 29—34).—Seven analyses are given of average commercial samples of gypsum rock and "dirt," which are quarried and mined in Kansas for the manufacture of cement. Besides calcium sulphate and water, the rock contains only small quantities of silica, iron oxide, alumina, magnesia, and carbonic anhydride. The "dirt," which is a light brown, soft, disintegrated material, is less pure. L. J. S.

Clay. By JEFFERSON MIDDLETON (*17th Ann. Rept. U.S. Geol. Survey* (for 1895—6), 1896, Part III., 816—880).—In this report on "the statistics of the clay-working industries of the United States," several analyses of clay, commercial felspar, &c., are given. L. J. S.

Permian and Triassic Rocks from near Liverpool. By PHILIP HOLLAND and EDMUND DICKSON (*Proc. Liverpool Geol. Soc*, 1896, **7**, 443—452).—Analyses are given of marls and sandstones of Permian and Triassic age from the neighbourhood of Liverpool; they were made

with the object of ascertaining the source of the rocks, and of determining the nature and amount of the cementing material. The fine material between the grains of the sandstones was separated and shown to consist mainly of small splinters of quartz, with some mica and felspar, but very little clay and no carbonates; traces of barium sulphate were sometimes present. L. J. S.

Meteoric Iron from Forsyth Co., Georgia. By EMIL W. COHEN (*Sitz.-Ber. Akad. Berlin*, 1897, 386—396. Compare Abstr., 1896, ii, 375).—This iron is remarkable, since it shows in the same mass two distinct structures; these are sharply separated from each other, but have intricate boundaries. One portion has a granular structure, and the grains, which are all $\frac{1}{4}$—$\frac{1}{2}$ mm. diam., themselves consist of grams 0·02—0·03 mm. diam., some of which are more readily etched than others; the other portion of the iron appears to be almost compact, and consists of grains 0·02 mm. across. The granular variety is easily etched by dilute acid, whilst the compact variety is only slowly attacked even by strong acids. Accessory constituents are comparatively rare, and are mostly confined to the compact portion; troilite is the most frequent, but graphite, schreibersite, and small, spindle-shaped bodies are also present. The iron, especially the granular variety, rusts very quickly, this being due to the presence of lawrencite, which oozes out on the surface in greenish drops and is then oxidised to ferric chloride and oxychloride. From the rust, 3·55 per cent. of chlorine was extracted by water, and 4·99 per cent. by sulphuric acid. Analyses were made by O. Sjöström of the granular (anal. I) and compact (II) varieties, taken from widely separated portions of the mass, and free from visible accessories and rust.

	Fe.	Ni.	Co.	Cu.	C.	S.	P.	Cl.	Total.
I.	94·18	5·56	0·60	0·02	0·04	0·05	0·19	0·17	100·81
II.	94·03	5·55	0·53	not est.	0·02	0·03	0·23	trace.	100·41

The granular portion was tested for manganese and chromium, but with negative results. The corresponding mineralogical composition is:

	Nickel-iron (Kamacite).	Schreibersite (Fe_2NiP).	Troilite (FeS).	Lawrencite ($FeCl_2$).	Sp. gr.
I. (Granular).	98·33	1·23	0·14	0·30	7·3357
II. (Compact).	98·42	1·49	0·08	0·01	7·4954

As the composition of the two varieties is essentially the same, the differences in sp. gr. and the action of acids can only be due to differences of structure. The low sp. gr. is due to the porosity of the iron, which is also indicated by the presence of enclosed gases.

Like the Locust Grove iron (this vol., ii, 272), this iron belongs to the rare group of meteorites called "ataxite" by the author. Accessories are small in amount, and apparently do not include cohenite, chromite and daubréelite. The differences in structure must be due to the rate of cooling, and the fragment found is probably only a portion of a mass originally larger. L. J. S.

The Bendegó Meteorite. By ORVILLE A. DERBY (*Archivos Museu Nacional, Rio de Janeiro*, 1896, 9, 87—184).—This iron, found in

1784, weighs 5360 kilos., and has the extreme dimensions 2·2 × 1·45 × 0·58 metres; it is now in the Rio de Janeiro Museum. Detailed accounts are given of the history and external form. Some planes of easy fracture, which mark the junctions of different crystalline individuals of the iron, are called "Wollaston planes." With the exception of troilite-nodules and patches of cohenite, the iron consists essentially of kamacite, there being very little tænite (about 0·1 per cent.) and probably no plessite, so that the Widmanstätten figures do not stand out in relief on the etched surface, but are visible as an oriented sheen. On the etched surfaces of the kamacite individuals are the so-called file markings, together with systems of fine raised lines, called "Bendegó lines," which are apparently due to lamellar twinning (parallel to the faces of the hexakisoctahedron {421}) as are the Neumann lines of hexahedral irons. Analysis of the bulk of the iron, which represents almost pure kamacite, gave I (by Dafert), and a partial analysis by G. Florence is given under II; this agrees with the usual formula, $Fe_{14}Ni$, for kamacite. The troilite gave the results under III (also a trace of silica); the residue probably consists of daubréelite and schreibersite. Cohenite is abundant, and is seen on the cut surface as embroidery-like patches; measurements by E. Hussak of the imperfect crystals show them to be isometric: sp. gr. 6·1805; analysis IV, by Dafert, after deducting 5·72 per cent. of schreibersite. The schreibersite and rhabdite gave analysis V (also a trace of tin); measurements are given of the tetragonal rhabdite needles. Analyses were made of another phosphide of iron and nickel of uncertain nature, which remains as a black powder when the iron is dissolved in dilute acid. Some chromite, rich in crystal faces, hypersthene and "magnetic globules" are also present. Carbon was shown to be absent in the gas evolved when the iron is dissolved in dilute acid.

	Fe.	Ni.	Co.	Cu.	P.	C.	S.	Insol.	Total.
I.	93·06	6·83		—	trace	—	—	0·33	100·22
II.	—	6·36	0·79	0·0045	—	—	—	—	—
III.	62·51	trace	trace	—	—	—	33·24	5·26	101·01
IV.	90·16	3·62		—	trace	6·39	—	—	100·17
V.	52·42	33·51		0·25	15·09	—	—	—	101·27

L. J. S.

[Hungarian Ores, Waters, &c.] By ALEXANDER VON KALECSINSZKY (*Jahresber. k. ung. geol. Anstalt*, 1894 (for 1892), 197—201; 1895 (for 1893), 170—176).—In these annual reports of the work done in the chemical laboratory of the Hungarian Geological Institute, analyses of rocks, ores, waters, coals, &c., are given. L. J. S.

Argentine Waters. By JUAN J. J. KYLE (*Anal. Soc. Cient. Argentina*, 1897, **43**, 19—25, 111—121, 161—171, 280—285).—The results of numerous analyses of waters from rivers, streams, surface and artesian wells in Argentina are given. L. J. S.

Physiological Chemistry.

The Relation of the Respiratory Exchanges to Temperature in Cold-blooded Animals. By HORACE MIDDLETON VERNON (*J. Physiol.*, 1897, **21**, 443—496).—In cold-blooded animals, the carbonic anhydride discharge does not vary directly with rise and fall of temperature. There are ranges in which metabolism remains nearly constant; this range is most marked in newts and earthworms, and comprises from 10° to 22·5° on warming, and a rather shorter range on cooling, the animals. The same is true for either a somewhat shorter or a somewhat different range in toads, blindworms, axolotls, and frogs. In *Rana temporaria*, the range is much shorter, 12·5° to 17·5°. In snails, the discharge increases from 2° to 20°, and then remains constant up to 30°. In the cockroach, the metabolism increases uniformly with the temperature.

In frogs, this was found to be due to a nervous mechanism in the bulb, since division of the brain above, and of the cord below the bulb, respectively do not and do abolish the range of constancy. Curare, however, unless given in excessive doses, does not abolish it. Morphine has but little action; strychnine causes a rapid increase of carbonic anhydride discharge on warming from 2° to 10°, but from this point up to 30° it remains constant. Veratrine causes the discharge to be constant up to 22°, beyond which point it increases much more rapidly than in normal frogs. Taking the average carbonic anhydride discharge of normal frogs from 2° to 30° as 1, that of the cockroach is 3·03, of the newt 1·6, of the toad 1·32, axolotl 1·14, snail 0·88, *Rana esculenta* 0·74, blindworm 0·52, earthworm 0·45, frogs with the cord divided just below the bulb 0·5 to 0·65, curarised frogs 0·43 to 0·58, according to the dose, strychnised frogs 2·56, and veratrinised frogs 1·22.

The mean respiratory quotient for both normal and curarised frogs is 0·85, frogs with the bulb divided at either its upper or lower border 0·94, strychnised frogs 1·22. The other animals examined had quotients varying from the maximal value of 0·9 for the earthworm to one of 0·72 for the blindworm. W. D. H.

Increased Absorption of Oxygen by the Blood, and the Therapeutic Use of Oxygen. By GEORG KASSNER (*Chem. Centr.*, 1896, ii, 307; from *Apoth. Zeitung*, **11**, 404—405).—The use of oxygen rather than compressed air is recommended in disease, as arguing principally from the high percentage of oxygen in the swimming-bladder of fishes, the blood appears to have the power of taking up more oxygen than nitrogen by absorption, and to take up more oxygen than is necessary for the life of the organism, such surplus being available on emergencies. W. D. H.

Osmotic Pressure as the Cause of Exchanges between Red Blood-corpuscles and Salt Solutions. By HANS KOEPPE (*Pflüger's Archiv*, 1897, **67**, 189—206).—The behaviour of red blood-corpuscles

in solutions of urea, ammonium carbonate, ammonium chloride, and other salts is in accord with the hypothesis that osmotic pressure comes into play between blood-corpuscles and blood-plasma, and that the osmotic pressure gives the measure of the volume of the blood discs. Small exceptions to this rule, noted when solutions of chloride and carbonate of sodium or potassium are employed, are explicable on the "theory of solutions" of van't Hoff and the "theory of electrical dissociation" of Arrhenius. W. D. H.

Physiological Action of certain Ethereal Salts. By G. VOGEL (*Pflüger's Archiv*, 1897, **67**, 141—162).—The following substances were injected intravenously in rabbits: ethylic formate, ethylic acetate, isobutylic acetate, amylic acetate, ethylic propionate, ethylic butyrate, isobutylic butyrate, ethylic valerate, amylic valerate, ethylic œnanthate, ethylic sebacate. In small quantities, they quickly cause an energetic increase of the respiratory activity. In large doses, they paralyse the nerve centres without preceding convulsions.

W. D. H.

Influence of β-Tetrahydronaphthylamine on the Body Temperature. By JOHN FAWCETT and W. HALE WHITE (*J. Physiol.*, 1897, **21**, 435—442).—Stern (*Virchow's Archiv*, 1889, **115**, 14) called attention to the fact that this drug causes a rise of temperature in rabbits. This is confirmed in the present research; 3 or 4 c.c. of a 3 per cent. solution injected under the skin causes pyrexia, a rise of from 2 to 5°, occurring within two or three hours. There is, simultaneously, increase in the rapidity of the heart and respiration. In animals poisoned by curare, or kept alive by artificial respiration after division of the spinal cord high up, this does not occur. Curare, and the operation, and even artificial respiration when the animal is etherised and tied down, produce a fall in temperature. The way in which the drug produces fever is therefore uncertain. It is, however, not due to increased muscular activity. W. D. H.

Changes which some Acids of the Oxalic Series undergo in the Organism. By PIO MARFORI (*Chem. Centr.*, 1896, ii, 106; from *Ann. Chim. Farm.*, **23**, 193—203).—Malonic acid, given either as such or as the sodium salt, passes only in small quantities into the urine; it leads to an increase of the urinary carbonates. Barbituric acid also arises from it, as oxaluric does from oxalic acid. Succinic acid does not pass into the urine. Glutaric acid passes only in small quantities into the urine; the greatest part is oxidised, and lessens the urinary acidity. No increase of volatile fatty acids was observed as the result of administering these dibasic acids. W. D. H.

Occurrence of Hydrogen Sulphide and Indole in the Human Stomach. By HERMANN STRAUSS (*Chem. Centr.*, 1896, ii, 109; from *Berl. klin. Woch.*, **33**, 385—389).—Certain cases of disordered digestion resulting from obstruction are described in which colonies of bacteria (of the *Bacterium coli* group) obtained from the stomach, produced indole and hydrogen sulphide. This can be produced in a peptone solution with or without the presence of sugar.

In other cases, hydrogen sulphide was absent, and the smell

produced was like that of putrid cheese. A back-flow of pancreatic juice into the stomach was suspected in some cases. W. D. H.

Action of Suprarenal Extracts. By SWALE VINCENT (*Proc. physiol. Soc.*, 1897, 25—26).—Large doses of extracts of the suprarenals of mammals, injected subcutaneously, cause death; the most marked symptom is muscular paralysis, of central origin. Blood in the urine, and from the nose, occasionally convulsions, and fall of temperature, were also observed. Glycerol extracts cause local ulceration. Extracts of the cortex of the gland, or of the liver, spleen, and kidney are inactive. After a sub-fatal dose, a partial immunity is set up. W. D. H.

Effect of Work on the Quality and Composition of Cows' Milk. By P. DORNIC (*Bied. Centr.*, 1896, **26**, 197—198; from *Milchzeit*, 1896, 331, and *L'ind. Latière*, 12 April, 1896).—Experiments lasting two weeks were made with two cows, which were used for ploughing for the first week, and rested the second week. During the period of work, the cows received, besides the usual food, 1 kilo. of rye per head per day. The effect of work on the composition of the milk was only slight. The dry matter and acid increased a little, whilst the yield of milk diminished slightly. The milk produced during the period of work frequently curdled at 45°, whilst that obtained during the period of rest curdled at 70—75°. N. H. J. M.

The Reason why Milk Coagulates when Heated. By BRUNO BARDACH (*Monatsh.*, 1897, **18**, 199—216).—About 12 hours' heating at 100° is necessary to coagulate quite fresh milk; at 150°, 3 minutes suffice. Most of the experiments were carried out at 130°, at which temperature 1 hour's heating is necessary. It was found that but the merest traces of volatile (formic) acid are formed; further, that the total acid formed is insufficient to coagulate the milk at the ordinary temperature. When a 5 per cent. solution of lactose is heated for 1 hour at 130°, no acid is formed; if 0·5 per cent. of sodium hydrogen phosphate is added in addition, then the reaction is found to have changed from alkaline to acid. A 4—8 per cent. solution of casein in water containing 0·4—0·8 per cent. of sodium hydrogen phosphate is unchanged when it is heated for a short time with the lactose solution that has been heated for an hour already; if the casein solution has also been heated for an hour previously, then coagulation at once takes place when the two solutions are heated together, and if a freshly made solution containing casein, lactose, and sodium hydrogen phosphate is heated for an hour, coagulation takes place. The coagulation that milk undergoes when heated is thus a complex process; coagulation is brought about by the action, at the high temperature, of the small quantities of acid formed from the lactose, but these are powerless to coagulate the original, unchanged casein, and it is only after the casein itself has also been changed by the heating that it becomes coagulated. C. F. B.

The Proteids of Cows' Milk. By KARL STORCH (*Monatsh.*, 1897, **18**, 244—281).—If cows' milk is freed from fat by skimming after it has remained for 24 hours, or after it has been centrifugalised,

and is then mixed with three times its volume of a saturated solution of sodium sulphate and a few drops of egg-albumin, and heated to 100°, coagulation takes place. When the filtrate from the coagulum is carefully neutralised with a saturated solution of sodium sulphate to which a very little acetic acid has been added, and is then stirred with excess of solid sodium sulphate, a substance, *a*, is salted out; in the filtrate from this, another substance, *b*, can be precipitated by the addition of strong acetic acid; if this is filtered off, the filtrate is now found to be free from proteids. If the milk, without previous coagulation, is at once saturated with solid sodium sulphate, *a* separates as before, and in the filtrate from it, acetic acid precipitates *b*, but the filtrate from this is now found to contain a proteid, which must be the lactalbumin of other authors (mixed, perhaps, with lactoglobulin, assuming that such a substance can really be obtained from milk). It is thus evident that, in the first method, the lactalbumin (and lactoglobulin) is removed by the preliminary coagulation. Both *a* and *b* contain phosphoric acid. *a* contains calcium, and is soluble in water; it is precipitated from the aqueous solution by the addition of acetic acid, but it is then free from calcium, and is insoluble in water, although soluble in very dilute solutions of alkalis; it has the character of a caseinogen, and is coagulated when it is warmed with rennet extract. *b* contains no calcium, and is insoluble in water, but soluble in very dilute alkalis; it is not appreciably coagulated by rennet.

As regards the power of salting out possessed by sodium sulphate, no precipitate can be obtained at the ordinary temperature when, not the solid salt, but a concentrated solution of it is used, no matter how much is added; at 50°, 19 volumes of the solution to 1 of the milk suffice to produce a precipitate; at 100°, 1 volume suffices. Magnesium sulphate may also be used for salting out; of a saturated solution of this salt, $1\frac{1}{2}$, $\frac{2}{3}$, and $\frac{1}{8}$ volumes suffice to produce a precipitate respectively at the ordinary temperature, 50°, and 100°. Sodium chloride may also be used; the numbers in this case are 8 and 2 volumes respectively at 50° and 100°; at the ordinary temperature, no precipitate can be produced by use of a saturated solution. When, however, magnesium sulphate or sodium chloride is used in the same way as sodium sulphate, *a* is found to be precipitated in the preliminary coagulation with egg-albumin, but the lactalbumin (and lactoglobulin) is not so precipitated, but remains in the filtrate from *b*. If, on the other hand, the preliminary coagulation is carried out with sodium sulphate and egg-albumin as at first, *a* can then be salted out from the filtrate with either magnesium sulphate or sodium chloride, and, in the filtrate from it, *b* can be separated as usual. In all cases the weight of *a* obtained is 0·47—0·56 gram from 20 c.c. of milk; of *b*, 0·05—0·08 gram.

After preliminary coagulation with sodium sulphate and egg-albumin, acetic acid produces a precipitate equal in weight to *a* and *b* together, and the filtrate contains no proteids. But a large quantity of acetic acid is necessary for this; otherwise the precipitation is only partial, and from the filtrate *a* and *b* can be obtained by successive treatment with sodium sulphate and acetic acid. The presumption is,

then, that the substance precipitated by acetic acid from the original milk is the true caseinogen, and that it is decomposed by metallic salts into the substances *a* and *b*. These two substances can be salted out together by saturating the milk with two of the salts at the same time; or one can be salted out with one salt, and, in the filtrate from it, the other can be salted out with another salt. C. F. B.

Action of Oxalic Acid and its Derivatives on the Kidneys. By WILHELM EBSTEIN and ARTHUR NICOLAIER (*Virchow's Archiv*, 1897, **148**, 366—388).—The investigation was undertaken with a view to the artificial production of urinary calculi. This was not accomplished, and the present communication relates to the action of oxalic acid and certain of its derivatives on the kidneys when administered in a succession of small doses to dogs and rabbits. Oxalic acid was found to cause the appearance of a deposit of calcium oxalate in the urinary tubules; these deposits are frequently visible to the naked eye. Oxamic acid is eliminated as a calcium salt in the urine. A similar result followed the administration of ammonium oxamate and oxamaethane; the kidneys were usually healthy. The administration of oxamide did not lead to the deposition of concretions; in many cases, the kidneys, however, were of the granular contracted kind. W. D. H.

The Work of Digestion and the Excretion of Nitrogen in the Urine. By N. V. RIAZANTSEFF (*Chem. Centr.*, 1896, ii, 746; from *Arch. des Sci. biol. St. Petersburg*, **4**, 393—414).—The increase in the urinary nitrogen which immediately follows a meal is believed to be due to the increased work of digestion. Foods which produce an increased activity of the secreting glands act in this way more efficaciously than those which produce less activity, but even acidified water (introduced, in a dog, into the stomach by a fistula) causes the glands to secrete, and this is followed by a rise in the nitrogen excreted in the urine. W. D. H.

Acetonuria. By FELIX HIRSCHFELD (*Chem. Centr.*, 1896, ii, 394—395; from *Centr. klin. med.*, **17**, 617—620).—In healthy persons, a diet of proteid and fat leads to an increase of acetone in the urine. The addition of carbohydrate to the diet causes this to disappear. This is explained by its "sparing" action on proteid metabolism. The same holds in the acetonuria of disease, and explains the occurrence of acetone in diabetics, in whom carbohydrate metabolism is upset. W. D. H.

Poisonous Action of Sulphurous Acid and its Salts, and the Admissibility of their Use in Foods. By HEINRICH KIONKA (*Chem. Centr.*, 1896, ii, 902; from *Zeit. Hyg.*, **22**, 351—397).—The "meat preserve crystals" prepared by Heyden and Co. contain 7·5 per cent. of sulphurous acid. This led to an investigation of this gas and its compounds as a poison. Contained in the inspired air, quite small quantities prove fatal. Small doses (0·02 to 0·04 gram) of sodium sulphite injected into frogs paralyse the heart, the central, and to some extent the peripheral nervous system. Dogs fed on the salt, or on food preserved by its use, suffer from injuries to various organs, especially

the lungs and kidneys; there is local irritation of the stomach, and a fall of blood pressure, and hæmorrhages tend to occur. The use of the salt as a preservative is most reprehensible. W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Fermentability of Galactose. By A. BAU (*Bied. Centr.*, 1896, **26**, 213—214; from *Zeit. Spiritus Ind.*, 1896, Nos. 38 and 39).—*d*-Galactose is not fermentable by *Saccharomyces productivus*, *S. membranæfaciens*, *S. apiculatus*, and *Schizosaccharomyces Pombe*. Under suitable conditions, it is completely fermented by *Saccharomyces cerevisiæ*, by *S. Logos*, *S. Pastorianus I*, *II*, and *III*, *S. ellipsoideus I* and *II*, *S. Marxianus*, lactose yeast, and also, but only slowly, by *Monila candida*. *d*-Galactose ferments with greater difficulty than *d*-glucose.

N. H. J. M.

Effect of Temperature on the Production of Free Oxalic Acid in Cultivations of Aspergillus niger (van Thiegh). By CARL WEHMER (*Bied. Centr.*, 1896, **26**, 191—192; from *Ber. deut. bot. Ges.*, 1896, 163).—*Aspergillus niger*, on peptone solution, produces free oxalic acid abundantly in presence of potassium, sodium, calcium, and ammonium nitrates, and ammonium phosphate, but not in presence of ammonium sulphate and chloride.

With ammonium nitrate, the amount of oxalic acid increases at 15—20°, and is gradually destroyed by the fungus. At 33—35°, free oxalic acid is no longer formed, but oxalates are sometimes found in small quantities. When calcium carbonate is added, calcium oxalate is produced in considerable amount, but under these conditions the fungus does not thrive.

When the fungus is cultivated on ammonium tartrate, the production of spores ceases at 33—35°. Oxalic acid could not be detected, and the liquid showed an alkaline reaction, the tartrate being converted into carbonate. In sugar solutions, free acid is formed in abundance at 8—10°, but is destroyed at a higher temperature (15°).

The change in amount of acid observed in *Crassulaceæ* during night and day is probably due to the change of temperature, the acid accumulating in the night and being destroyed in the daytime.

N. H. J. M.

Latent Vitality of Seeds. By J. GIGLIOLI (*Ann. Agron.*, 1897, **23**, 190—191; from *La Nature*, 1895, **52**, 544).—A number of seeds were kept for 15 years in various gases. Seeds of lucerne, wheat, vetch, and coriander completely lost the power of germinating when kept in hydrogen, which was probably not absolutely dry. The following percentage of lucerne seeds germinated after being kept in the different gases. In oxygen, 0·68 per cent.; nitrogen, 56·56; chlorine and hydrogen chloride, 6·2; hydrogen sulphide, 0·99;

hydrogen arsenide, 70·98 and 68·82; carbonic oxide, 84·2; nitrogen peroxide, 0·97 and 0·62 per cent. None of the seeds kept in carbonic anhydride germinated, possibly owing to the presence of too much moisture.

After being kept in different alcoholic solutions, the following amounts of lucerne seed germinated: alcohol, alone 66·6 per cent.; concentrated solution of mercuric chloride, 20·2; sulphurous acid, 0·15; hydrogen sulphide, 7·03; nitrogen peroxide, 4·16. In alcoholic solutions of chloroform and phenol, all the seeds were destroyed. Many of the seeds which germinated were planted, and produced normal plants.

If the gases and the seeds had been more thoroughly dried, more of them would probably have retained their vitality. N. H. J. M.

Nitrogen Assimilation in the Cotton Plant. By CHARLES E. COATES and W. R. DODSON (*Journ. Amer. Chem. Soc.*, 1896, **18**, 425—428).—Experiments were made to ascertain whether the cotton plant, which, like the *Leguminosæ*, is highly nitrogenous, can assimilate free nitrogen.

The plants were grown in pots each containing about 6 lbs. of ignited white sand, with and without minerals. Pots 1—2 had nothing added; pots 3—4 had mineral food; pots 5—7 had minerals, and, in addition, 25 c.c. of soil extract (from cotton soil, and containing in 25 c.c. N = 0·0003 gram).

In pots 1, 2, and 3, the plants died in three or four weeks, apparently from nitrogen starvation. The plant of pot 4 stopped growing after about six and a half weeks and lived two weeks longer, when it was taken up; the plants of pots 5 and 6 were taken up at the same time, having stopped growing. The following analytical results show that, under the conditions of the experiments, there was no fixation of nitrogen, either with or without soil extract, the slight gain being within the limits of experimental error. The results are in grams:

	Pot 4.	Pot 5.	Pot 6.	Pot 7.
Nitrogen in seed sown	0·004	0·0038	0·0039	0·0036
Nitrogen found in seed (? in total produce *)	0·0068	0·0056	0·0074	0·0080
Dry matter in seed (? in total produce)	0·5050	0·4768	0·8350	0·9664

N. H. J. M.

Relation between the Transpiration of Plants and the Concentration of the Nutritive Solutions. By B. HEINRICH (*Ann. Agron.*, 1897, **23**, 186—187; from *Ber. Landw. Versuchs.-Stat. Rostock*, 1895, **2**, 170).—In a damp atmosphere, oats evaporated 102 grams of water per gram of dry substance, whilst in dry air the water evaporated amounted to 618 grams.

In order to ascertain the effect of the concentration of nutritive solutions on evaporation, oats were grown in solutions containing different amounts of a mixture corresponding with the formula

* This would accord with the gain of nitrogen as given in the text: N = 0·0028, 0·0018, 0·0035, and 0·0044 gram.

$4HK_2PO_4 + CaCl_2 + 5Ca(NO_3)_2 + 2MgSO_4 + Fe_2Cl_6$. The following results were obtained:

Strength of solution per cent............	3	1	0·5	0·25	0·1
Dry produce (grams)....................	134	74	44	28	18
Evaporation (c.c. per gram of dry produce)	515	550	684	688	629

The evaporation increased up to the period of flowering, after which it diminished. The results recall those of Hellriegel (*Ann. Agron.*, **11**, 59), who showed that, according to the amount of calcium nitrate supplied, barley evaporated from 250 to 800 c.c. of water per gram of dry substance. (Compare also Dehérain, *ibid.*, **18**, 465.)

N. H. J. M.

Migration of Calcium Phosphate in Plants. By L. VAUDIN (*Ann. Agron.*, 1897, **23**, 232—233; from *Ann. Inst. Pasteur*, 1895, 636).—The results of previous experiments having shown that in presence of alkali malates, the sugars may keep calcium phosphate in solution, it seemed possible that the organic acids of plants may have a share in assisting the migration of calcium phosphate. The phosphoric acid of the stems of wheat accumulates in the seeds at the time of maturation, and migrates from the seeds, when they germinate, towards the organs in course of development.

An examination of aqueous extracts of wheat grain and ears at different periods, from the time when the ears formed (June 15) to the time of cutting, showed the presence of malic acid in the ears in June, succinic and malic acids in July, whilst in August the seeds contained a small amount of succinic acid, but no malic acid. The acidity (as P_2O_5) in June was 0·75, and in August 0·286 per cent. on the dry substance.

The dry grain contained 1·6 per cent. of sugar, and traces of succinic acid. During germination, starch is converted into sugar, and the succinic acid is replaced by malic acid. The calcium phosphate thus becomes soluble. When the sugars of the grain are converted into starch, succinic acid appears (produced, probably, from the malic acid, which disappears at the same time). During this period of maturation, the calcium phosphate becomes insoluble, owing to the decomposition of the solvents, sugar and malic acid; there is thus a simultaneous deposition of calcium phosphate and of starch.

Malic acid is found also in maize and barley at the time when the ears are formed; and, like wheat, ripe barley grains contain succinic acid. In leguminous plants, citric acid has the same *rôle* as malic acid in cereals.

N. H. J. M.

Composition and Analysis of Wheats. By AIMÉ GIRARD (*Compt. rend.*, 1897, **124**, 926—932).—Since the bye-products of the manufacture of flour are largely used as feeding stuffs for stock, it follows that the same general principles should be applied in their analysis as in that of the whole wheat and the flour (this vol., ii, 382). The chief point is to separate the nitrogenous constituents from the carbohydrates of the woody fibre, but at present no process is known which permits this to be done completely and accurately. In order to separate the starch from the integuments, &c., of the seeds, the bye-

products are mixed with ten times their weight of ice-cold water, and subjected for 20 hours to the action of an agitator with paddles, the temperature being kept at 0°. The liquid is afterwards passed through a sieve, which arrests everything but the starch and gluten. The latter are dried and weighed, and afterwards separated in the manner previously described (*loc. cit.*). If this separation is found to be difficult owing to the physical condition of the gluten, it should be mixed with a definite quantity of flour from the same wheat, the proportions of starch and gluten in which have already been determined.

In order to determine the soluble matter, the best plan is to agitate the substance with ice-cold water, as in the determination of the starch and gluten, the liquid being filtered and the soluble matter determined in the filtrate. Agitation for 4 hours is sufficient.

When estimating the fat, it is advisable to adopt the plan recommended by the author some years ago, of treating the material with a 5 per cent. solution of hydrochloric acid, and again drying before treating with benzene. Since some of the fat is removed during the mechanical separation of the starch and gluten, a separate estimation of the fat in the residue is desirable. Indirect estimations of cellulose and the like are unsatisfactory, and it is better to make a direct determination of the nitrogenous and inorganic matter on the residue from which starch and gluten have been separated.

Analyses of the bye-products from four French wheats (*loc. cit.*) gave the following results: Water, 14·33 to 15·12. *Matter soluble in water*: proteids, 2·48—2·92; carbohydrates, 5·74—6·58; inorganic matter, 1·50—2·04. *Matter insoluble in water*: gluten, 4·31—4·78; starch, 26·36—29·79; nitrogenous woody matter, 4·88—6·52; fats, 2·68—3·65; celluloses, 29·06—31·38; inorganic matter, 1·81—2·12; loss, &c., 0·66—1·75 = 100.

The composition of the whole wheat was as follows: mean weight of a grain, 0·038 to 0·051 gram; kernel, 83·04 to 85·98; germ, 1·16 to 1·50; envelope, 12·52—15·61 = 100; water, 14·50—15·12; gluten, 6·64—7·13; soluble diastases, &c., 1·37—1·74; lignoses, 1·46—1·95; starch, 56·84—58·78; fats, 1·58—1·81; sugars, 0·75—1·33; galactin, 0·36—0·69; other soluble carbohydrates, 1·77—1·97; celluloses, 8·88—9·56; inorganic matter, 1·49—1·54; loss, &c., 0·74—1·94 = 100.

C. H. B.

Physiological Study of the Cyclamen. By ALEXANDRE HÉBERT and G. TRUFFAUT (*Bull. Soc. Chim.*, 1897, [iii], **15**, 850—855).—A study of the changes of weight and composition produced in the different organs of the plant when grown in different kinds of soil.

M. W. T.

Lime and Lupins. By HEINRICH (*Bied. Centr.*, 1896, **26**, 231—232; from *Deut. landw. Presse*, 1896, No. 91, 809 and 816).—The results of the addition of 0·5, 1, 5 and 10 per cent. of chalk to sandy soil in which lupins were grown, showed that even the smallest amount was injurious to the plants, whilst with 10 per cent. the amount of dry produce was reduced from 150 grams to 27 grams. Gypsum (1 per cent.) reduced the produce to about half. Calcium phosphate (0·5 per cent.) was injurious, whilst in larger quantity (1 per cent.) it

completely destroyed the vegetation. Magnesium carbonate (0·5 per cent.) also killed the plants.

The injurious effect of calcium carbonate is to some extent diminished, but not eliminated, by the addition of kainite, or sodium nitrate. N. H. J. M.

Mineral Constituents of the Watermelon. By GEORGE F. PAYNE (*J. Amer. Chem. Soc.*, 1896, **18**, 1061—1063).—The watermelon contains about 0·3 per cent. of mineral matter, containing

SO_3.	CaO.	MgO.	K_2O.	Na_2O.	SiO_2.	P_2O_5.	Cl.	Fe_2O_3.	Total.
4·41	5·54	6·74	61·18	4·31	2·15	10·25	4·94	0·48	100.

In selecting a suitable manure, the grower must pay particular attention to the amount of potash, which should largely exceed the phosphoric acid. L. DE K.

Effect of Manure on the [Botanical] Composition of Crops. By H. A. MORITZ FLEISCHER (*Bied. Centr.*, 1897, **26**, 161—164; from *Mitteil. Ver. Förd. Moorkultur in Deut. Reich.*, 1896, No. **23**, 441).—Whilst it is generally acknowledged that the application of nitrogenous manures to meadows induces an increased growth of the grasses, and, in consequence, a decrease of leguminous herbage, it is still uncertain what effect phosphoric acid, and potash, respectively have on the relation between the amount of *Gramineæ* and *Leguminosæ*. Maercker assumes that it is potash, and not phosphoric acid, which promotes the growth of leguminous plants rather than that of the grasses (Mentzel and von Lengercke's, *Landw. Kalender*, 1897, 69).

The results of experiments made on peaty land showed an increase in the percentage of *Leguminosæ* only after the simultaneous application of potash and phosphates, but it seems to be more important to apply large amounts of phosphoric acid than large amounts of potash. Whilst potash (150 kilos. per hectare) in conjunction with basic slag (50 and 100 kilos.) raised the percentage of leguminous herbage by 14·9 and 30·4 per cent. respectively, the percentage was increased by 28·29 after application of basic slag (100 kilos.) and potash (75 kilos.), and the addition of greater amounts of potash had no essential effect.

It is concluded that, on peaty soil, phosphoric acid is at least as important as potash in increasing the growth of the *Leguminosæ*, and that it must be of still greater importance in the case of ordinary mineral soils. The Rothamsted experiments, which Maercker quotes (*loc. cit.*) as supporting his view, do not include plots manured exclusively with potash. N. H. J. M.

NOTE.—Although there is no exclusively potash plot in the grass experiments at Rothamsted, the results of botanical separations of the herbage of plots receiving mineral manures, including and excluding potash, show conclusively that it is the potash and not the phosphoric acid to which increased growth of the *Leguminosæ* must be attributed. The following is a summary of results obtained in 1877 from a few plots :—Plot 3 (unmanured since 1856), plot 7 (complete minerals since

1856), plot 8 (complete minerals 1856—1861, but without potash since), and plot 4[1] (superphosphate 1859 and since).

	Plot 3.	Plot 7.	Plot 8.	Plot 4[1].
Gramineæ	71·75	74·38	81·19	71·78
Leguminosæ	8·54	13·71	4·01	5·53
Miscellaneous	20·31	11·91	14·80	22·69

N. H. J. M.

Relative Manurial Value and the Preservation of the Nitrogen of Stable Manure. By JULIUS H. AEBY, R. DORSCH, FR. MATZ and PAUL WAGNER (*Landw. Versuchs.-Stat.*, 1897, **48**, 247—360).—A large number of vegetation and other experiments are described from which the following conclusions are drawn. The nitrogen of stable manure is utilised to a considerably less extent than that of ammonia and nitrates, and to a less extent than that of green manure. Whilst the nitrogen of fæces and litter acts very slowly, the nitrogen of urine is very rapidly converted into ammonia, especially in presence of fæces, and the straw of cereals. The abundant application of fresh fæces immediately before sowing quickly growing plants, may give rise to diminished production owing to the liberation of free nitrogen which would otherwise be available to the plant. Destruction of nitrates is brought about by stable manure, as well as by fresh fæces, and even, although extremely slowly, by garden soil, by arable soil containing humus, and by the straw of cereals. The decomposition of nitrates by fæces is increased by addition of straw.

For every 100 parts of nitrogen in fæces and litter, stable manure receives not less than 100 parts of urine-nitrogen; in practice, however, stable manure does not usually contain more than 25 to 35, frequently only 10, parts of the urine-nitrogen for every 100 parts of fæces- and litter-nitrogen. This is owing to the separation of liquid manure, to loss as ammonia, and to elimination of free nitrogen.

Formation of ammonia in mixtures of fæces and straw is so slow that it need not be taken into account. When such mixtures are kept in layers of 80 to 100 cm. high, only slight changes take place during 12 months when it is trodden down. If turned over so as to admit air, decomposition takes place which may result in a loss of 50 per cent. of the organic matter. The usual preservatives (gypsum, superphosphate and kainite) mixed with the manure in the usual quantities have no effect on the process of humification.

As humification proceeds, the power of destroying nitrates diminishes, and it is probable that the better results obtained with rotten manure as compared with fresh manure is essentially connected with the diminished power of decomposing nitrates.

Carbon bisulphide applied to stable manure renders it unable to destroy nitrates, but the process is practically useless owing to the amount of bisulphide required and the length of time necessary for its action. Sulphuric acid and copper sulphate both act vigorously on the micro-organisms of stable manure, but it remains to be seen whether their use is practicable. N. H. J. M.

Decompositions during the Putrefaction of Nitrogenous Organic Matter. By F. W. THEODOR C. PFEIFFER, E. FRANKE, C.

GÖTZE and H. THURMANN (*Landw. Versuchs.-Stat.*, 1897, 48, 189—245).—In the first series of experiments, the loss of nitrogen in cow's excrement (mixed with peat), both alone, and after admixture of gypsum, and of gypsum with superphosphate, respectively, was determined under the following conditions. (1) The manures were kept in two sets of flasks through both of which air was passed twice a week for five months, and through one of which air was passed continuously for five months longer. (2) The manures were kept in zinc boxes, (*a*) in a compressed and (*b*) in a loose state, for five months.

The next series of experiments were made to ascertain the effect of sulphuric acid (0·3 to 1 per cent.), superphosphate, potassium fluoride, and calcium hypochlorite respectively on the ammoniacal fermentation in solutions of urea, and of urea mixed with peat litter and liquid manure. The mixtures were kept for five months in bottles through which air was drawn continuously.

A third set of experiments was made to study the effect of lime and calcium carbonate on denitrification. Fresh horse-dung (100 grams), both alone and after addition of (1) lime (1 and 3 grams), (2) calcium carbonate (1 and 3 grams) respectively with a mixture of butyric, capric, and caproic acids (0·5 gram), and (3) sulphuric acid (0·5 gram), was kept for some weeks with 0·25 per cent. nitrate solution (1500 c.c.) in loosely stoppered bottles at the ordinary temperature, and the amount of nitrate determined from time to time.

In a fourth series, the amount of ammonia formed at the ordinary temperature, and at 30—32°, in peat saturated with urine and liquid manure, without further addition, and with addition of superphosphate, lime, calcium carbonate, and butyric acid, &c., respectively was determined. The manures were kept in bottles through which air was drawn continuously. The ammonia determinations were made at intervals of from two weeks to two months during the six months which the experiments lasted.

A series of pot experiments was made in which oats were grown in sandy soil (N = 0·062 per cent.), manured with potassium nitrate alone, with horse-, sheep- and cow-dung respectively, both alone and with addition of (1) potassium nitrate, (2) potassium nitrate and lime, (3) potassium nitrate and marl. The total produce and nitrogen in the produce were determined.

The following conclusions are drawn from the results of the various experiments:

Loss of nitrogen did not occur to any great extent when air has only limited access to the decomposing substance, but with increased and prolonged aëration as much as 42·6 per cent. of the total nitrogen was lost.

The effect of preservatives was uncertain. When used under conditions of vigorous aëration, the loss of nitrogen, although lessened, was nevertheless greater than the loss without preservatives and with less aëration. The mechanical treatment of manure is therefore of far greater importance than the use of chemical preservatives. In most of the experiments, the nitrogen lost was in the free state. Losses of ammonia were relatively slight.

The presence of lime (2 per cent.) prevented the denitrifying action

of fresh horse-dung on nitrate solution, whilst calcium carbonate (3 per cent.), and sulphuric acid (0·5 per cent.) had no effect. In vegetation experiments, 3 per cent. of lime, or 5 per cent. of marl, sufficed to limit the denitrifying action of cow-dung.

Oxidation of ammonia was only hindered by addition of sufficient superphosphate to completely combine with it. This result is, however, not opposed to the observed favourable effect of the addition of small quantities of superphosphate to manure, since in practice the oxidation of ammonia would be much less vigorous than in these experiments.

Addition of lime or calcium carbonate to decomposing manure at the ordinary temperature almost completely stopped the liberation of free nitrogen, and this gain exceeded the increased loss of ammonia. It is probable that loss of free nitrogen in stable manure might be diminished by layers of lime or marl, whilst loss through evolution of ammonia might possibly be to some extent hindered by covering the manure heap with soil.

Ammoniacal fermentation was rather increased than diminished by addition of large amounts of lime or superphosphate, and was only slightly hindered by 1 per cent. of sulphuric acid. N. H. J. M.

Analytical Chemistry.

Detection of Halogens in Organic Compounds. By J. H. Kastle and W. A. Beatty (*Amer. Chem. J.*, 1897, 19, 412—414).—About 0·1 gram of the substance to be examined is heated in a test-tube with about 0·5 gram of a mixture of silver and copper nitrates and a few drops of water until the nitrates are completely decomposed, the temperature not being allowed to rise above a dull red heat. Dilute sulphuric acid is added to the residue, and then zinc; after 5—10 minutes, the liquid is filtered, and tested with silver nitrate and nitric acid for the presence of halogens. If a volatile substance has to be examined, the tube employed is 6 × ¼ inches long, closed at one end, and divided into three roughly equal parts by two bends at right angles. About 0·25 gram of the substance is introduced into the closed end, and the tube is clamped with the limb next the open end pointing slightly upwards; about 0·5 gram of the dry, mixed nitrates is then introduced into the bend at the end of this limb, and the substance and nitrates are heated alternately (the former very gently) until all the substance has volatilised, and all the nitrates are decomposed; the residue is then examined as before. C. F. B.

Estimation of Oxygen dissolved in Sea Water. By Albert Lévy and Félix Marboutin (*Compt. rend.*, 1897, 124, 959—961).—One of the authors described some time ago a method of estimating oxygen in natural waters by allowing it to oxidise a standard ferrous solution, the excess of ferrous salt being afterwards determined by means of permanganate solution. With spring or river water, the

results are identical with those obtained by extracting the gas as such, and they are the same whether permanganate or dichromate solution is used for the final titration. With sea-water, however, it is difficult to obtain accurate results with permanganate owing to the liberation of chlorine, but dichromate gives results identical with those obtained by the pump. Magnesium compounds do not interfere if the precipitate and liquid are thoroughly mixed. C. H. B.

Estimation of Sulphur in Cast-Iron. By FRANCIS C. PHILLIPS (*J. Amer. Chem. Soc.*, 1896, **18**, 1079—1086.)—About 1·5 gram of of the finely powdered and sifted metal is mixed with 8 grams of a mixture of 45 parts each of sodium dioxide and sodium nitrate, together with 10 parts of sodium carbonate; or 4 grams each of sodium nitrate and carbonate may be employed. On heating, a somewhat violent action occurs, and after 20 minutes the contents are fully oxidised. After cooling, the mass is softened in water, the solution decanted, and the residue ground, while wet, in a mortar. The solution and residue are then digested in a beaker on the water bath for 1 hour, after adding 2 c.c. of strong bromine water. The filtrate is acidified with hydrochloric acid, any silica is removed by evaporating to dryness, and the sulphuric acid is finally determined in the usual manner.

When testing ferromanganese, it is better to use a mixture of equal parts of sodium nitrate, and carbonate, omitting the sodium peroxide; under these circumstances, sodium manganate is not formed. Some grey irons cannot be crushed or ground; to these, the method is not applicable, but in their case the evolution method answers all requirements. L. DE K.

Optical Method for the Estimation of Sulphuric Acid. By AGLOT (*Bull. Soc. Chim.*, 1897, [iii], **15**, 855—862).—This method depends on the opacity produced by the addition of barium chloride to a solution of sulphuric acid, as measured by means of an apparatus described by the author in another paper. Accurate results can only be obtained in alcoholic solution, impurities vitiate the results. M. W. T.

Modification of the Gunning Method for Nitrates. By JOHN FIELDS (*J. Amer. Chem. Soc.*, 1896, **18**, 1102—1104).—From 0·7 to 3·5 grams of the sample is introduced into a 250—500 c.c. digestion flask, and 30 c.c. of sulphuric acid containing 1 gram of salicylic acid is added, and the whole gently heated to dissolve the nitrates; 6—7 grams of potassium sulphide is then added in small portions, the flask being well shaken after each addition. The heat is now rapidly increased until the mixture boils, and after the end of an hour the liquid is allowed to cool; it is then diluted, rendered alkaline, and the ammonia distilled off in the usual manner.

The chief advantage of the modification appears to be the short time of boiling and the obviation of frothing. L. DE K.

Quantitative Separation of Arsenic and Antimony. By OSCAR PILOTY and ALFRED STOCK (*Ber.*, 1897, **30**, 1649—1655).—The substance is placed in a round-bottomed flask of about 300 c.c. capacity,

and is then dissolved in 100 c.c. of concentrated hydrochloric acid, the flask is fitted up as if for steam distillation, except that the longer tube is provided with a T-piece at its upper extremity to allow of the introduction of both hydrogen chloride and hydrogen sulphide gases, and that the shorter tube is bent and passes into a receiver of about 600 c.c. capacity surrounded with ice. The contents of the round flask are heated to boiling, and a rapid stream of hydrogen chloride is passed through. When the whole apparatus has become filled with steam, the hydrogen sulphide is admitted at the rate of about two small bubbles per second. The distillation is continued until only a few c.c. of liquid remain in the flask, an operation which requires $\frac{1}{2}$—$\frac{3}{4}$ of an hour. All the arsenic is found in the receiver in the form of the trisulphide, mixed with free sulphur; it is collected, dissolved in as little dilute potash as possible, and then oxidised with bromine water, a slight excess of hydrochloric acid is added, and the contents of the flask briskly boiled until all traces of free bromine have disappeared. The clear hydrochloric acid solution is then heated at 70° for 3 hours while a stream of hydrogen sulphide is passed through, the gas is also kept passing through as the solutions cools, and the saturated solution is then put aside for 12 hours, when the arsenic pentasulphide may be collected on to a Gooch crucible, washed with water, absolute alcohol, pure carbon bisulphide, alcohol, and dry ether, then dried at 105° and weighed. The antimony may be estimated in the clear solution left in the round-bottomed flask by precipitating as sulphide, and treating in exactly the same way as the arsenic pentasulphide. The results are correct, and the complete operation occupies but 9 hours. It presents several advantages over E. Fischer's method (*Annalen*, 1881, **208**, 186), or the various modifications suggested by Hufschmidt, or by Classen and Ludwig (Abstr., 1885, 932). It is also much quicker than the method suggested by Friedheim and Michaelis (Abstr., 1895, ii, 415). J. J. S.

Estimation of Carbon in Pig Iron. By BERTRAND S. SUMMERS (*J. Amer. Chem. Soc.*, 1896, **18**, 1087—1091).—The old oxygen combustion process has never been excelled as regards accuracy, but with refractory residues the time required for a combustion may be about 3 hours, which renders the process unsuitable to works chemists.

The author has substituted a platinum tube for the usual porcelain or glass tube, and uses a specially constructed purifying and absorption apparatus, for details of which the original paper should be consulted. The chief characteristic is that rubber connections are avoided, the only rubber in use being at the ends of the combustion tube.

An analysis may be completed in something like 20 minutes.

L. DE K.

Simplification of Organic Elementary Analysis. By MAXIMILIANO DENNSTEDT (*Ber.*, 1897, **30**, 1590—1597).—The author's method of analysis admits of the simultaneous determination of carbon, hydrogen, sulphur, and halogen. The combustion tube is 83 cm. in length, and rests in an iron trough which is heated by Teclu burners, the usual form of combustion furnace being discarded. A layer of platinum black, 6—8 cm. long, occupies the middle of the tube, the

organic compound being weighed in a platinum or porcelain boat placed at a convenient distance from the metal; the usual form of apparatus for absorbing carbonic anhydride and water is attached to the end of the tube, and the combustion is carried out from the beginning in an atmosphere of oxygen. Supposing the substance to contain carbon, hydrogen, nitrogen, sulphur, and halogen, there are inserted between the platinum black and absorption apparatus four weighed boats, two of silver foil containing molecular silver, the others being of porcelain, and filled with lead peroxide. Then the increase in the weight of the silver boats is regarded as halogen and SO_4, whilst the lead peroxide boats take up NO_2 and SO_2; the lead peroxide must then be extracted with 33 per cent. alcohol to remove lead nitrate, the quantity of which is thereby determined. From these data the percentage of carbon, hydrogen, sulphur, and halogen may be calculated.

M. O. F.

Ferrocyanides of Zinc and Manganese. By EDMUND H. MILLER (*J. Amer. Chem. Soc.*, 1896, **18**, 1100—1102).—A preliminary note regarding the composition of metallic ferrocyanides. The author is of opinion that when titrating a zinc solution by means of potassium ferrocyanide, the precipitate does not consist of pure zinc ferrocyanide, but that it invariably contains potassium.

The pure compound can only be obtained by the direct action of hydrogen ferrocyanide on zinc oxide; the same is the case with manganese.

The author recommends a hydrochloric acid solution of platinic chloride as a very satisfactory indicator during the titration. It is used in the same way as uranium acetate, in a hot solution. The end reaction is a bright emerald-green which takes a few seconds to develop.

L. DE K.

Estimation of Mercury. By GEORGES DENIGÈS. (*Bull. Soc. Chim.*, 1897, [iii], **15**, 862—871).—To a solution containing any mercuric salt, a known quantity of potassium cyanide is added. After addition of ammonia and some potassium iodide, the mixture is titrated with decinormal silver nitrate solution, the appearance of silver iodide indicating the end of the reaction. The quantity of mercuric salt can be calculated from the equation: $2n\text{KCN} + m\text{HgX}'' + (n-m)\text{AgNO}_3 = m\text{Hg(CN)}_2 + \text{K}_2\text{X}'' + n - m\text{AgCN,KCN} + (n-m)\text{KNO}_3$. The reaction, as might be expected, is not quite complete, and consequently a correction must be applied to the results.

M. W. T.

Microchemical Reaction for Didymium. By FEDERICO CHAVES Y PÉREZ DEL PULGAR and FEDERICO RELIMPIO Y ORTEGA (*Anal. Soc. Españ. Hist. Nat.*, 1895, **24**, Actas 75—77).—The crystals obtained with potassium ferrocyanide in the method described by Behrens are figured and described; they consist of a hexagonal prism and basal plane with rounded faces, and are sometimes twinned. The optical characters conform with the hexagonal symmetry, and the birefringence is strong.

L. J. S.

Separation of Manganese from Tungstic Acid; Estimation of Molybdenum. By WALTER T. TAGGART and EDGAR F. SMITH (*J.

Amer. Chem. Soc., 1896, **18**, 1053—1054).—The authors state that manganese chloride cannot be separated from sodium tungstate by means of yellow ammonium sulphide in the presence of ammonium chloride; no better results were obtained by using a solution of potassium carbonate. It is, however, probable that fusion with an alkali carbonate might be successful.

In the course of an analysis, molybdenum is often obtained as sulphide, which it is difficult to convert into a weighable form. The authors find that the dry sulphide, when ignited with anhydrous oxalic acid, rapidly burns to the pure trioxide. L. DE K.

Separation of Vanadium from Arsenic. By CHARLES FIELD and EDGAR F. SMITH (*J. Amer. Chem. Soc.*, 1896, **18**, 1051—1052).—The authors have found that arsenic may be completely separated from vanadium by heating the mixed sulphides in a current of hydrogen chloride at a temperature not exceeding 250°.

The arsenic is completely volatilised, whilst the vanadium is left behind in the boat. The method, in addition to being satisfactory from an analytical point of view, certainly forms a very excellent means of freeing vanadium from arsenic. L. DE K.

Metal Separations by means of Gaseous Hydrogen Chloride. By J. BIRD MOYER (*J. Amer. Chem. Soc.*, 1896, **18**, 1029—1044).—The author calls attention to the use of gaseous hydrogen chloride in analysis. The most convenient way of preparing it is to drop sulphuric acid from a tap funnel into strong hydrochloric acid contained in a 3-litre flask. The gas is then dried by passing it through two wash bottles containing sulphuric acid, and finally through a calcium chloride tower. The substance to be acted on is weighed out in a porcelain boat, and the latter is placed in a combustion tube made of hard glass.

The oxides of antimony, bismuth, and arsenic are completely volatilised as chlorides at a temperature varying from 130° to 180°, whilst those of lead, copper, cadmium, zinc, silver, nickel, and copper are not volatilised at that temperature, so that their chlorides remain in the boat and may be weighed. Copper oxide is, however, but superficially acted on, and, if it is mixed with bismuth oxide, it should be dissolved in a little hydrochloric acid before heating it in the current of hydrogen chloride to volatilise the bismuth.

The process is, therefore, a very convenient one for the separation of antimony, arsenic, or bismuth from any of the others. When iron is present it cannot be employed, as it is very difficult to prevent the volatilisation of a little ferric chloride. The only drawback seems to be the very long time (average 7 hours) necessary to expel the volatile chlorides. L. DE K.

Solubility of Bismuth Sulphide in Alkali Sulphides. By GEORGE C. STONE (*J. Amer. Chem. Soc.*, 1896, **18**, 1091).—Stillman (this vol., ii, 127) has proved that when a solution of a bismuth salt is neutralised with aqueous soda and then heated with excess of sodium sulphide, a considerable amount of bismuth sulphide dissolves in that reagent.

The author confirms this statement, but he also finds that bismuth sulphide precipitated from an acid solution by means of hydrogen sulphide is not soluble when heated with excess of an alkali sulphide.

L. DE K.

Separation of Bismuth from Lead. By ARTHUR L. BENKERT and EDGAR F. SMITH (*J. Amer. Chem. Soc.*, 1896, **18**, 1055—1056).—The authors state that bismuth may be completely separated from lead by boiling the nearly neutralised solution with excess of a solution of sodium formate containing a little formic acid. The precipitate contains a little lead from which it may be completely freed by redissolving in nitric acid and precipitating a second time. The basic bismuth formate thus obtained is then dissolved in dilute nitric acid, and precipitated as usual with ammonium carbonate. L. DE K.

Quantitative Testing of Ethereal Oils. By SCHIMMEL AND CO. (*Chem. Centr.*, 1896, ii, 977—978; from Schimmel and Co.'s *Bericht*, 1896, October. Compare Abstr., 1895, ii, 333—540).—Bergamot oil has a sp. gr. = 0·882—0·886 at 15°, and a rotatory power = +8° to +20° at 15—20° (100 mm. tube). The specific gravity is reduced by adulteration with turpentine oil, citron oil, orange oil, alcohol, and distilled bergamot oil, whilst fatty oils, cedar-wood oil and gurjun balsam oil increase it. The pure oil dissolves in half a part or more of 90 per cent. alcohol, but 80 per cent. alcohol does not form a clear solution with all oils, probably owing to the presence of wax-like substances introduced into the oil by pressing the rind. The residue after evaporation amounts to 5—6 per cent., and consists mostly of bergaptene; more than 6 per cent. residue indicates the presence of fatty oil. The essential constituent of the oil is linalylic acetate, $C_{10}H_{17}OAc$, which amounts to 30—40 per cent. This is determined by boiling 2 grams of oil with 10 c.c. of semi-normal alcoholic potassium hydroxide solution for half an hour and determining the excess of alkali in the cold solution after addition of water by means of semi-normal sulphuric acid, using phenolphthalein as indicator. The percentage of acetate x is formed from the formula $x = g \div 19{\cdot}6\frac{y}{2}$, where y is the number of c.c. of alkali used and g the weight of oil taken.

Oil of lemon has a sp. gr. = 0·858—0·861 at 15°, and the rotatory power at 20° = +59° to +67°, usually only 64° (the difference in the angle of rotation at temperatures from 10—20°, for 1° = −9′, from 20—30° = −8·2°). Adulteration with turpentine oil alone is easily detected by the decreased rotation. The presence of orange oil with turpentine oil may be proved by slow distillation, when the first distillate which contains the pinene of boiling point lower than that of limonene, possesses a considerably lower rotatory power than that of the original oil.

Orange oil has a sp. gr. = 0·848—0·852 at 15°, and a rotatory power at 20° = +96° to +98° (100 mm. tube). All adulterants, such as turpentine oil, alcohol, and oil of lemon, cause a considerable reduction of rotatory power. Turpentine oil may be recognised by the same method as that used in the case of oil of lemon.

Lavender oil has a sp. gr. = 0·883—0·895 at 15°, and the rotatory power at 20° = −4° to −8° (100 mm. tube). The pure oil forms a

clear solution in three times its volume and more of 70 per cent. alcohol. Linalylic acetate with some geranylic acetate is the main constituent of the oil. The former is determined as in the case of bergamot oil, and should amount at least to 30 per cent.; very good oils contain 40 per cent. and more.

In oil of cloves, methylic alcohol and furfuraldehyde have been detected; the latter is perhaps the cause of the darkening of various ethereal oils.

In American peppermint oil, amylic alcohol and small quantities of sulphur compounds, probably for the most part dimethylic sulphide, were detected.

Oil of rue has a sp. gr. $= 0\cdot833$—$0\cdot840$, and a rotatory power $= +0° 13'$ to $+2° 10'$ (100 mm. tube). The pure oil forms a clear solution in 70 per cent. alcohol, and solidifies at 8—10° in consequence of the separation of its main constituent, methyl nonyl ketone.

French or Italian oil of rosemary has a sp. gr. of more than 0·900, and a slight dextrorotatory power. The pure oil forms a clear solution in half a part and more of 90 per cent. alcohol, as also in 10 parts of 80 per cent. alcohol. E. W. W.

Chemico-legal Detection of Alkaloids and Narcotic Substances. By ALBERT HILGER and K. JANSEN (*Zeit. anal. Chem.*, 1897, **36**, 344—346; from *Forschungsber. über Lebensmittel*, **1**, 14, 30).—The authors have applied the method of Küster (*Zeit. anal. Chem.*, **29**, 118) to the separation of the above substances. The method consists in treating the material to be examined with alcoholic tartaric acid, evaporating the filtered extract with plaster of Paris, and extracting the powdered mass, first in an acid condition, and then after making alkaline, with ether and with chloroform in a Soxhlet extractor.

Strychnine is not extracted by ether, whether acid or alkaline. Chloroform extracts notable proportions from the acid mass, but the greater part after rendering alkaline. When strychnine or brucine has been mixed with decomposed animal matter, the ethereal extracts contain only ptomaines. When potato or beer is present, the ethereal extract from the acid mass will contain solanidine or hop-resin, the alkaline ether extract, and the chloroform extracts contain the alkaloids.

From animal and vegetable matters mixed with atropine, the acid ether extracts only traces of the alkaloid; the acid chloroform extracts the bulk of the atropine. The alkaline extracts contain only traces.

Veratrine is extracted by both solvents, from both acid and alkaline masses, but chloroform is the better solvent.

Colchicine and digitalin are best extracted by chloroform after making alkaline, although traces are extracted in the other three cases.

Morphine is not extracted by either solvent from an acid mass, but both solvents, as well as amylic alcohol, remove it from the alkaline mass.

The extracts containing the alkaloids are as a rule colourless.

M. J. S.

General and Physical Chemistry.

Chemical Action of Light. By JOHN GIBSON (*Zeit. physikal. Chem.*, 1897, 23, 349—354).—The author contends that in all cases the chemical action of light is such that the new products have a higher conductivity than the original. Thus the effects on selenium, sulphur, phosphorus, and mercuric sulphide are all of this nature. By the combination of hydrogen and chlorine, and the decomposition of silver and mercury salts, the resulting products have increased conductivity. Under the influence of light, lead oxide changes to the peroxide, and manganous hydrate oxidises, in each case with increase of conductivity. The action on solutions of chlorine, potassium iodide, and bromine is of the same nature, but an apparent exception is found in the case of nitric acid, which is decomposed by light. This is, however, not an exception, as the conductivity of nitric acid solutions increases up to 32 per cent., when the maximum is reached, whilst the decomposition by light ceases when the concentration has fallen to 47 per cent. Other examples are also given, but the author points out that this simple and general law may be masked by secondary reactions between the products initially formed.

L. M. J.

Action of Light on Gaseous Mixtures, with Special Reference to Hydrogen and Chlorine. By ARMAND GAUTIER and H. HÉLIER (*Compt. rend.*, 1897, **124**, 1128—1133).—The experiments were made with pure hydrogen prepared in the usual way, and chlorine prepared by the action of hydrochloric acid on manganese peroxide precipitated by dilute nitric acid from solutions of the (?) "bichloride." Whether dry or moist, the two gases do not combine in the dark, no matter how long they may remain in contact.

Direct experiments showed that practically no combination of the two gases takes place under the influence of the light of a candle equivalent to 0·1 of a carcel, and placed at a distance of 1 metre, and only traces of hydrogen chloride are formed even after exposure to this light for several days, provided the gases are pure and dry.

C. H. B.

Isomerism of Position and Rotatory Power. By PHILIPPE A. GUYE (*Bull. Soc. Chim.*, 1896, [iii], 15, 1157—1160).—From the results of Frankland and Wharton (Trans., 1896, 1309 and 1583) and others, it appears that para- derivatives are more active than meta-, and meta- more active than ortho-. This result is in harmony with the relative position of the centre of gravity in the several groups, but, as the author points out, the variation of the product of asymmetry might occur in such a manner that the ortho-compound would exhibit the greatest, and the para-compound the smallest activity. From the relative position of the centre of gravity in the different groups, it might be inferred that a compound containing the phenyl group would have a greater or smaller rotatory power than a compound containing the tolyl group. This is, however, not always the case, as the phenyl

derivative sometimes occupies an intermediate position among the three tolyl derivatives, showing that the constitution as well as the mass of a substituting group influences the rotation. H. C.

Two Methods for the Measurement of the Dielectric Constant and Electrical Absorption with Rapid Vibrations. By PAUL DRUDE (*Zeit. physikal. Chem.*, 1897, **23**, 267—325).—The more rapid vibrations are more convenient than the ordinary slower discharges owing to their applicability in the case of conductors. The method first described consists of the determination of the ratio of the wave-length in air and in the liquid examined. An ordinary form of Hertzian oscillator is employed, and the position of the nodes determined (1) when the wires are in air, (2) when they pass through a trough of the liquid. For non-absorbing liquids, the dielectric constant is given by the square of this ratio, in the case of absorbing liquids by $r^2(1-a^2)$ where a is the absorption coefficient. For conductors, the absorption coefficient can be calculated from the conductivity, but in the case of liquids showing anomalous absorption, that is, which absorb, but do not conduct, the absorption was determined by the preparation of aqueous solutions of equal absorbing power, as shown by the number of nodes observable. In the second method, condensers, filled with (1) air, (2) the compound required, were, by means of an adjustable length of wire, brought into resonance with the oscillator and their capacities, and in this way the dielectric constant was determined. This method could also be employed for solids, and is well adapted for finding the temperature coefficient, and for rare liquids. The results of the author for varying mixtures of methylic alcohol and water give a perfect, unbroken line, and thus differ from those obtained by Thwing, which exhibited many breaks. Unbroken or regular curves in close agreement with the numbers calculated by the mixture rule were obtained also for propionic acid and water, acetone and benzene, and acetone and water. A large number of liquids and solids were examined, and tables are given, but the results are frequently not in accord with those of other observers. This, however, is in many cases probably due to the difference in the wave-length, as experiments with acetaldehyde, benzaldehyde, acetone, and diethyl ketone show the variability of the dielectric constant with the wave-length, that is, measure the electric dispersion. The connection between the anomalous dispersion and chemical constitution is also discussed, the effect being apparently indicative of hydroxyl groups (see this vol., ii, 303).
L. M. J.

Influence of Proximity of Substances on Voltaic Action. By GEORGE GORE (*Phil. Mag.*, 1897, [v], **43**, 440—457).—The author has, on a previous occasion, shown that the difference of pressure due to gravity at the upper and lower ends of a vertical column of an electrolyte about 3 metres high, on two perfectly similar electrodes of the same metal at the upper and lower ends of the column, produced a very feeble current. If gravity, by producing pressure, exerts an extremely minute influence on chemical and voltaic action, similar effects, although excessively minute ones, must be produced by the gravitative action of a large mass of metal or other substance on a

voltaic electrode at the end of a horizontal column of electrolyte presented to it. Experiments confirming this view are described in the paper. H. C.

Effect of Great Current-strength on the Conductivity of Electrolytes. By THEODORE W. RICHARDS and JOHN TROWBRIDGE (*Phil. Mag.*, 1897, [v], **43**, 376—378).—As the authors' method of determining resistance by measuring its damping effect on electric oscillations applies to electrolytes, provided that the resistance to be measured is less than 20 ohms, experiments were made to ascertain whether the intense current involved in the discharge of a large condenser is capable of causing any change in the condition of an electrolyte. It was found that the resistance of concentrated copper sulphate and zinc sulphate solutions is not essentially altered by great alterations in the strength of the current. That the strong instantaneous current, which alters so much the resistance of gases, has so little effect on solutions, is no doubt due to the great mass and specific heat of the material, which must be warmed in the latter case. H. C.

Thermo-electric Properties of some Liquid Metals. By WILLIAM BECKIT BURNIE (*Phil. Mag.*, 1897, [v], **43**, 397—410).—Tin, lead, bismuth, and mercury were each thermo-electrically compared with copper, the tested metal being contained in a hard glass tube, so that the observations could be pushed to temperatures considerably above those of the melting metals, and the changes in the thermo-electric properties during the process of melting observed. About the melting point, a small variation of temperature produces a considerable change in the direction of the thermo-electric curve. The effect is smallest with lead, with tin it is larger, and with bismuth it is very remarkable, that metal changing during melting from an exceedingly active thermo-electric metal to one very similar to lead in its thermo-electric properties. With mercury, also, a great change takes place at the melting point. H. C.

Heats of Vaporisation of Liquids. By S. ROSLINGTON MILNER (*Phil. Mag.*, 1897, [v] **43**, 291—304).—The author shows that the internal heat of vaporisation of a liquid may be expressed by the formula, $L_i = \frac{RT}{JM}\left\{\frac{1}{0{\cdot}4343}\log_{10}\frac{v'-b}{v-b} + \frac{b}{v-b} - \frac{b}{v'-b}\right\}$ in which v and v' are the specific volumes of the liquid and saturated vapour respectively. The quantity b, although not constant, has a value satisfying van der Waals's equation, $(p + a/v^2)(v - b) = RT/M$, v being the volume of the liquid and a an absolute constant. H. C.

Dynamics of Homogeneous Endothermic and Exothermic Chemical Reactions. By MICHEL PETROVITCH (*Compt. rend.*, 1897, **124**, 1344—1346).—A calculation of approximate relationships between temperature, time, and the masses of reacting substances in any homogeneous system in which chemical changes are taking place. H. C.

Gradual Change and Thermodynamics. By PIERRE DUHEM (*Zeit. physikal. Chem.*, 1897, **23**, 193—266).—The author investigates

at considerable length the thermodynamical equations applicable to the case of the slow alteration of a substance which tends to reach a final natural state. Such a slow change is well illustrated in the case of sulphur, for which the freezing point is a maximum when the sulphur is previously kept at a temperature of 121°. On the assumption that the melted sulphur gradually changes to a modification containing the element in two states, and that the freezing point depends on the ratio of these, the author applies his previous thermodynamical deductions to the sulphur changes. The velocity of solidification of overcooled melted sulphur at any particular temperature varies according to its previous history, and the dependence of this velocity on (1) the temperature of the melted sulphur, (2) the time during which it was kept at this temperature, and (3) the time of overcooling are all proved to be in accord with the theoretical deductions. The velocity of the change from monoclinic to rhombic sulphur is, in a similar manner, dependent on the previous history, and the results are again found to be in accord with the theory. The changes in monoclinic sulphur when kept for a long time at the ordinary temperature and the effect of repeated crystallisations are considered, and also the slow changes of rhombic sulphur at different temperatures and the effect of repeated melting and solidification. The author finally investigates the cyclical change by which the sulphur finally returns to its original state, and shows that in this case the well known Clausius inequality holds good.

L. M. J.

Reduction of the Freezing Point of an Aqueous Solution. By A. Ponsot (*Bull. Soc. Chim.*, 1896, [iii], **15**, 1073—1078. Compare Abstr., 1896, ii, 636.)—The author describes the ideal conditions which should be as far as possible maintained in determining the freezing points of dilute solutions, the prevention of any loss of heat by radiation from the solution being one of the most important. He criticises Raoult's conclusions on this subject.

H. C.

Means of Recognising a Good Method of Cryoscopy. By A. Ponsot (*Compt. rend.*, 1897, **124**, 1227—1230).—A mathematical discussion of the influence of superfusion on determinations of the freezing points of solutions, and the correction thereby rendered necessary.

C. H. B.

Heat of Formation of Zinc Hydroxide. By Gustave Massol (*Bull. Soc. Chim.*, 1896, [iii], **15**, 1104—1105).—Since

$$C_3H_4O_2 + ZnO \text{ sol.} = +15{\cdot}37 \text{ Cal.}$$
$$C_3H_4O_2 + Zn(OH)_2 \text{ sol.} = +11{\cdot}05 \text{ Cal.}$$

and the heat of fusion of $H_2O = -1{\cdot}43$ Cal., it follows that

$$ZnO \text{ sol.} + H_2O \text{ sol.} = Zn(OH)_2 \text{ sol.} + 2{\cdot}89 \text{ Cal.}$$

The heat of hydration of zinc oxide is therefore exothermic, as is the case with most other oxides.

J. J. S.

Thermochemistry of the Sodioacetylenes. By Camille Matignon (*Compt. rend.*, 1897, **124**, 1026—1028).—The violent action of water on the sodioacetylenes was regulated by placing the compressed substance in a small inverted glass vessel which was immersed in the

calorimeter. In some experiments, the sodioacetylene was decomposed by dilute hydrochloric acid and in others by water.

C_2HNa sol. + HCl diss. = C_2H_2 gas + NaCl diss. develops + 28·3 Cal.
C_2HNa sol. + H_2O = C_2H_2 gas + NaOH diss. develops + 14·5 Cal.

and it follows that

C_2(diamond) + H + Na sol. = C_2HNa sol. absorbs − 29·2 Cal.

Further:

C_2Na_2 sol. + 2HCl diss. = C_2H_2 gas + 2NaCl diss. develops + 64·96 Cal.
C_2Na_2 sol. + $2H_2O$ = C_2H_2 gas + 2NaOH diss. develops + 37·6 Cal.

and hence

C_2(diamond) + Na_2 sol. = C_2Na_2 sol. absorbs − 8·8 Cal.

It follows that

C_2H_2 gas + Na = C_2NaH sol. + H develops + 28·9 Cal.
C_2H_2 gas + Na_2 = C_2Na_2 sol. + H_2 develops + 49·3 Cal.

The thermal value of the first hydrogen is comparable with that of the alcoholic function of the tertiary alcohols; the value of the second hydrogen is distinctly lower.

Both the sodium derivatives are endothermic and retain part of the energy of the acetylene molecule, which they resemble in decomposing with liberation of carbon when their temperature is raised rapidly. When pure, they can be handled without danger, and are not sensitive to percussion or friction, but if mixed with oxidising agents they become violently explosive and as a rule are sensitive to friction.

C. H. B.

Heat of Formation of Sodioacetylenes. By ROBERT DE FORCRAND (*Compt. rend.*, 1897, **124**, 1153—1155).—If Matignon's results (preceding abstract) are recalculated with + 43·08 Cal. as the value of the reaction Na + Aq, the numbers + 28·58, + 48·56, and + 19·98 are obtained instead of those given by Matignon (+ 28·9, + 49·3, and + 20·4) who probably took Na + Aq = + 43·45 Cal.

Matignon's conclusion that the thermal value of the first displaceable hydrogen approximates to that of tertiary alcohols, can only be arrived at if the heat of solidification of the acetylene is neglected. From Villard's results on the heats of formation of hydrates of gases, and the known heat of solidification of carbonic anhydride, it seems very probable that the heat of solidification of acetylene is about + 6·54 Cal., and if this value is adopted, the following results are obtained:

C_2H_2 sol. + Na sol. = C_2HNa sol. + H gas	develops	+ 22·04 Cal.
C_2H_2 sol. + Na_2 sol. = C_2Na_2 sol. + H gas	,,	+ 42·02 Cal.
C_2HNa sol. + Na sol. = C_2Na_2 sol. + H gas	,,	+ 19·98 Cal.
$\frac{1}{2}C_2H_2$ sol. + Na sol. = $\frac{1}{2}C_2Na_2$ sol. + H gas	,,	+ 21·01 Cal.

It is clear that, when calculated on this basis, the thermal value of the first hydrogen is considerably less than that of tertiary alcohols. At the same time, it is also clear that the difference between the first and second hydrogen is much greater than can be attributed to experimental errors, but many analogous cases are known. C. H. B.

Calculation of the Calorific Power of Coals by Dulong's Law. By GEORGES ARTH (*Bull. Soc. Chim.*, 1896, [iii], **15**, 1112—1116. Compare *ibid.*, 1895, [iii], **13**, 820).—The author has examined 13 specimens of coal from *Bascoup* (*ibid.*, [iii], **7**, 478) and finds that in each case the calorific power as determined by experiment agrees with that deduced from Dulong's formula. J. J. S.

Calculation of the Coefficient of Expansion of Gases based on a Theory of Valency. By JOACHIM SPERBER (*Zeit. anorg. Chem.*, 1897, **14**, 374—378).—The author makes use of his theory of valency (this vol., ii., 307) for the purpose of calculating the coefficient of expansion of certain diatomic gases. In this way, the coefficients of expansion of fluorine, chlorine, bromine, and oxygen are found to give values that differ but slightly from 0·00365. H. C.

Variation of the Dissociation Coefficient with Temperature. By S. ROSLINGTON MILNER (*Phil. Mag.*, 1897, [v], **43**, 286—290).—A proof of the law of the variation of the dissociation coefficient with temperature, first worked out by van't Hoff. H. C.

Non-concentrating Solutions. By WILHELM MEYERHOFFER (*Ber.*, 1897, **30**, 1810—1812).—Certain solutions in contact with the dissolving substance undergo no further concentration on evaporation, but if water is removed from the system at all, this water is lost by the solid salt and not by the solution. This is the case with any solution in contact with ice, and in many systems in which an aqueous solution is in contact with a hydrated salt. In the latter case, if the solutions are saturated, they form points on a curve connecting two multiple points of different order, a triple point with a quadruple point, or a quadruple point with a quintuple. Such curves have a temperature maximum in the lower multiple point. H. C.

Solubilities of Several Readily Soluble Salts. By FRANZ MYLIUS and ROBERT FUNK (*Ber.*, 1897, **30**, 1716—1725).—The authors have determined the solubilities of several readily soluble salts which had hitherto not been studied. The results are correct to 1 per cent. The finely divided salt was shaken with water at 18° for at least an hour, the excess of salt was allowed to subside at the same temperature, and a portion of the clear solution was removed by a pipette, weighed, and analysed.

In the Table, *a* gives the most stable form of the compound in the presence of the solution at 18°. The molecules of salts of lithium, sodium, and potassium, with monobasic acids, are doubled in order that the numbers in column *e* may be comparable, *b* gives the sp. gr. of the saturated solutions, *c* the percentage of anhydrous salt in the solution, *d* the amount of salt in grams dissolved in 100 grams of water, and *e* the number of molecules of water to one molecule of anhydrous salt in the solution, *f* gives the melting point of the salt of the formula given in the first column, *g* gives the number of molecules of water required to dissolve one molecule of the salt, and *h* the water of crystallisation expressed as percentage of the water required for solution.

Magnesium iodate occurs in the anhydrous form and also crystal-

—	—	a.	b.	c.	d.	e.	f.	g.	h.
1	Lithium chlorate	$(LiClO_3)_2$	1·815	75·8	313·5	3·2	125°	3·2	0
2	Calcium chlorate	$Ca(ClO_3)_2+2H_2O$	1·729	64	177·8	6·5	part under 100°	4·5	31
3	Lithium chromate	$Li_2CrO_4+2H_2O$	1·574	52·6	110·9	6·7	about 185°	4·7	30
4	Zinc chlorate	$Zn(ClO_3)_2+6H_2O$	1·914	65	186·2	7	60°	1	87
5	Potassium fluoride	$(KF)_2+4H_2O$	1·502	48	92·3	7	about 46°	3	57
6	Calcium nitrate	$Ca(NO_3)_2+4H_2O$	1·548	54·8	121·2	7·4	44°	3·4	54
7	Magnesium chlorate	$Mg(ClO_3)_2+6H_2O$	1·594	56·3	128·6	8·2	40°	2·2	74
8	Zinc nitrate	$Zn(NO_3)_2+6H_2O$	1·664	53·9	116·9	9	36·4°	3	67
9	Strontium chlorate	$Sr(ClO_3)_2$	1·839	63·6	174·9	9·3	does not melt.	9·3	0
10	Lithium bromate	$(LiBrO_3)_2$	1·833	60·4	153·7	9·8	,,	9·8	0
11	Magnesium bromide	$MgBr_2+6H_2O$	1·655	50·8	103·4	9·9	about 165°	3·9	61
12	Magnesium iodide	MgI_2+8H_2O	1·909	59·7	148	10·4	about 45°	2·4	77
13	Magnesium nitrate	$Mg(NO_3)_2+6H_2O$	1·384	43·1	75·7	10·8	about 94°	4·8	56
14	Magnesium chromate	$MgCrO_4+7H_2O$	1·422	42	72·3	11	part under 100°	4	64
15	Lead chlorate	$Pb(ClO_3)_2+H_2O$	1·947	60·2	151·3	13·7	does not melt.	12·7	7·3
16	Sodium chromate	$Na_2CrO_4+10H_2O$	1·409	38·1	61·4	14·6	24°	4·6	69
17	Lithium iodate	$(LiIO_3)_2$	1·568	44·6	80·3	25·2	does not melt.	25·2	0
18	Sodium fluoride	$(NaF)_2$	1·044	4·3	4·4	104·8	,,	105	0
19	Magnesium iodate	$Mg(IO_3)_2+4H_2O$	1·078	6·44	6·88	292	,,	288	1·4
20	Calcium iodate	$Ca(IO_3)_2+6H_2O$	1	0·25	0·25	868	,,	862	0·7
21	Lithium fluoride	$(LiF)_2$	1·003	0·27	0·27	1038	,,	1038	0

lised with $4H_2O$ when deposited by slowly cooling a warm saturated solution. A supersaturated solution, when cooled to 0° and well stirred, yields rhombic plates containing $10H_2O$. When a small quantity of this hydrate is warmed, it melts at 50° to a clear liquid; on cooling to 0°, the liquid becomes syrupy, but does not crystallise again unless rubbed with a glass rod. When the liquid is kept at 50° for several seconds, or for a longer time at the ordinary temperature, water is given up and crystals of the hydrate $Mg(IO_3)_2 + 4H_2O$ are deposited. The solubility of the hydrate $Mg(IO_3)_2 + 10H_2O$ increases rapidly with the temperature. A saturated solution at 0° contains but 3·1 per cent. of anhydrous salt, whereas a saturated solution at 50° contains 67·5 per cent.

The only hydrate of zinc iodate which could be obtained was $Zn(IO_3)_2 + 2H_2O$ which, according to Rammelsberg, requires 114 parts of water for solution.

The authors have obtained the hydrate $Ca(IO_3)_2 + 6H_2O$ described by Rammelsberg, but not the hydrate $Ca(IO_3)_2 + 4H_2O$ described by Ditte. When the hydrate $Ca(IO_3) + 6H_2O$ is suspended in water and the mixture heated to boiling, it is converted into the hydrate $Ca(IO_3)_2 + H_2O$.

Saturated solutions of the hydrate $Ca(IO_3)_2 + 6H_2O$ at

	0°	10°	18°	30°	40°	50°	54°	60°
contain...	0·1	0·17	0·25	0·42	0·61	0·89	1·04	1·36

per cent. anhydrous salt.

Saturated solutions of the hydrate $Ca(IO_3)_2 + H_2O$ at

	21°	35°	40°	45°	50°	60°	80°	100°
contain...	0·37	0·48	0·52	0·54	0·59	0·65	0·79	0·94

per cent. anhydrous salt. J. J. S.

Influence of Water on the Solubility in Ether of Certain Compounds. By HUGO SCHIFF (*Zeit. physikal. Chem.*, 1897, **23**, 355—356).—Phloretin is soluble in water to the extent of 0·12 per thousand and in ether to the extent of 4 per thousand. By the addition of 1 per cent. of water to the ether, the solubility increases to 50 per thousand and by saturation of the ether with water it again decreases to 35 per thousand. This increase by addition of water cannot be due to the formation of alcohol, in which phloretin is easily soluble, as the addition of 1 per cent. of alcohol to the ether only raises the solubility to 24 per thousand (compare Boedtker, this vol., ii, 367). L. M. J.

Velocity of Solidification. By GUSTAV TAMMANN (*Zeit. physikal. Chem.*, 1897, **23**, 326—328).—The velocity of solidification of overcooled sulphur and phosphorus was found by Gernez to be proportional to the overcooling. Experiments with salol, benzoic anhydride, benzophenone, diphenylamine, α-naphthylamine, hydrocinnamic acid, and azobenzene, however, showed that, although the velocity is at first so proportionate, yet with further overcooling the velocity becomes constant. When the overcooling is so great that the heat developed by the solidification does not raise the temperature to the freezing point, the velocity again decreases greatly. This is the case for benzophenone for an overcooling of 90° and at a temperature of $-40°$; melted

benzophenone does not solidify when touched by a small portion of the solid, whilst if then slowly heated, solidification proceeds, but at first with very small velocity. For phosphorus, for which the heat developed by solidification is sufficient to raise the temperature 26°, the velocity of solidification at 0° is only 1/100 of the velocity at 24°, the lowest temperature investigated by Gernez. The maximum velocity is independent of the containing vessel, and is, the author states, a characteristic constant for each substance. L. M. J.

Application of the Laws of Chemical Equilibrium to Complex Inorganic Compounds. By WILHELM MEYERHOFFER (*Ber.*, 1897, **30**, 1804—1809).—Friedheim (Abstr., 1894, ii, 314) has prepared a number of complex inorganic compounds by the action of alkali phosphates or arsenates on chromates and sulphates. These compounds he regards, not as molecular compounds, but as formed of complex molecules of definite atomic structure. This view the author opposes in the present paper, showing that the formation of these compounds takes place under conditions precisely analogous to those which hold generally for the formation of those double salts which are usually regarded as molecular compounds. H. C.

Precipitation of Organic Compounds by Bases. By MARCEL LACHAUD (*Bull. Soc. Chim.*, 1896, [iii], **15**, 1105—1108).—Dextrin is partially precipitated from its aqueous solutions by the addition of magnesia or any of the alkaline earth carbonates, but at the same time a part of the precipitating agent goes into solution. Similar results are obtained when solutions of such salts as aluminium sulphate, chrome alum, ferric sulphate or lead nitrate are added to a solution of dextrin and then rendered alkaline with ammonia. Extended experiments with dextrin, ferric sulphate, and ammonia showed that the whole of the dextrin can be precipitated if the ferric hydroxide is in large excess; if, however, the dextrin is in large excess, no precipitate is formed, and all the iron remains in solution. Many other organic compounds behave in much the same way as dextrin. J. J. S.

Precipitation of Dextrin by Soils. By MARCEL LACHAUD (*Bull. Soc. Chim.*, 1896, [iii], **15**, 1108—1110).—The author finds that different vegetable soils are capable of precipitating dextrin from its solutions, and the same is true of gelatin solutions, but even to a greater extent. The amount precipitated is greater in the case of a barren soil or of a soil which has been calcined than with an ordinary fertile soil. J. J. S.

Study of Capillary Affinity. By MARCEL LACHAUD (*Bull. Soc. Chim.*, 1896, [iii], **15**, 1110—1112).—Animal charcoal absorbs atmospheric moisture, the amount absorbed depending on the specimen of charcoal, and also on the temperature.

In the case of solutions, equilibrium is only slowly established if the charcoal is coarse and of compact texture; if, however, the charcoal is fine and light, equilibrium is established in 30—40 minutes. The chief factor in all cases of absorption is the strength of the solution. With mixtures of different solutions, the action of animal charcoal differs considerably according to the nature of the solutions; in most

cases, the charcoal exerts a selective absorbing action. Salicylic acid is absorbed more readily than any of its salts, and the absorption of the salts increases roughly with the molecular weight of the salt. It is impossible to give any exact method for estimating the values of animal charcoals. J. J. S.

A New Laboratory Turbine. By HEINRICH C. TRYLLER (*Ber.*, 1897, **30**, 1729—1731).—A turbine is described in which the ordinary form of propeller is replaced by a disc of iron wire gauze. The machine is more easily regulated, works more quietly, and requires less water than those constructed on the old principle. M. O. F.

A New Extraction Apparatus. By EMIL DIEPOLDER (*Ber.*, 1897, **30**, 1797—1798).—The new apparatus is an improvement on the form described by Schwarz (*Zeit. anal. Chem.*, 1884, **23**, 369). The vessel which contains the aqueous solution is a tall cylinder, and from the surface of the liquid the extracting agent is syphoned by means of a side-tube which leads into a distilling flask, the contents of which can be boiled. The vapour is then led to the condenser, from which the distillate passes to the bottom of the cylinder, and works up through the aqueous solution to the surface. Obviously, this form is applicable only in the case of specifically light extracting agents. When the liquid employed has a density greater than that of water, the syphon tube leads to the bottom of the cylinder, and the distillate is returned to the surface of the liquid.

A figure illustrates the proportions of the apparatus. M. O. F.

Inorganic Chemistry.

Liquefaction of Fluorine. By HENRI MOISSAN and JAMES DEWAR (*Compt. rend.*, 1897, **124**, 1202—1205).—Fluorine under atmospheric pressure does not liquefy at $-183°$, the temperature of liquid oxygen boiling under atmospheric pressure, but if the pressure on the oxygen be reduced so that the temperature falls to about $-185°$, the fluorine condenses to a very mobile, yellowish liquid, the colour of which resembles that of a long column of the gas.

Fluorine at these low temperatures has no action on glass, and if silicon, boron, carbon, sulphur, phosphorus, or iron is cooled in liquid oxygen and then thrown into an atmosphere of fluorine, it does not take fire, nor is iodine displaced from iodides. Benzene and terebenthene, however, are decomposed with incandescence if the temperature exceeds $-180°$, and hence it would seem that the attraction of fluorine for hydrogen is the last to disappear at low temperatures.

When gaseous fluorine is passed into liquid oxygen, a white, flocculent precipitate forms rapidly, and if collected on a filter it deflagrates violently as soon as its temperature rises. This product is under investigation.

C. H. B.

Composition of Nitrogen Chloride. By W. HENTSCHEL (*Ber.*, 1897, **30**, 1792—1795).—The author's modification of Balard's method of preparing nitrogen chloride consists in mixing solutions of ammonium chloride and sodium hypochlorite, and extracting the product with benzene. If the quantity of ammonium chloride is limited, solutions of chlorine in nitrogen chloride are obtained, and are found to be of indefinite composition, but a homogeneous product is always formed if the molecular proportion of ammonium chloride to chlorine is equal to or greater than 2 : 3 ; the compound then has the normal composition, NCl_3, even if the proportion just indicated reaches 16 : 3.

A sketch of the apparatus employed for determining nitrogen in nitrogen chloride is given in the paper. M. O. F.

Action of Water on Phosphoryl Chloride. By J. ADOLPHE BESSON (*Compt. rend.*, 1897, **124**, 1099—1102).—When a current of moist air is passed through phosphoryl chloride, metaphosphoryl and pyrophosphoryl chlorides are formed as well as phosphoric acids, and the same result follows when cold water is allowed to fall drop by drop into well cooled phosphoryl chloride. The products are difficult to isolate, but when distilled under very low pressure the residue consists of phosphoric acid and metaphosphoryl chloride, whilst the distillate consists of the pyrophosphoryl chloride mixed with some unaltered phosphoryl chloride. At 110°, pyrophosphoryl chloride decomposes into phosphoryl and metaphosphoryl chlorides, and the latter at a higher temperature splits up into phosphoryl chloride and phosphoric anhydride. Pyrophosphoryl chloride, $P_2O_3Cl_4$, does not solidify at $-50°$; it dissolves very rapidly in water with production of a slight turbidity which, however, disappears almost immediately. The regulated action of water on phosphoryl chloride yields pyrophosphoryl chloride, metaphosphoryl chloride, and phosphoric acid in proportions which vary with the conditions. The author has previously obtained, by the action of hydrogen sulphide on phosphoryl chloride, a compound, $P_2O_2SCl_4$, which is analogous to pyrophosphoryl chloride, $P_2O_3Cl_4$ (this vol., ii, 208). C. H. B.

Graphite, Graphitite, and Graphitoid. By ERNST WEINSCHENK (*Zeits. Kryst. Min.*, 1897, **28**, 291—304. Compare Abstr., 1892, 406; 1893, ii, 320, &c.).—From a review of the evidence put forward for the existence of graphitite and graphitoid as distinct modifications or varieties of graphite, and from his own observations made on natural and artificial material, the author considers that there is no essential difference between these and graphite, and that they must therefore be taken as being identical with the latter.

The property of not swelling up when moistened with nitric acid and ignited, on which the name graphitite was based, is explained by the crystals of "graphitite" being smaller and more compact, and therefore freer from cleavage cracks into which the acid could penetrate. The so-called graphititic acid has been obtained in crystals having the outlines of the original graphitite, and with the same optical characters as graphitic acid. Graphitic acid has also been prepared from graphitoid. There is no difference between the readiness with which graphite and

graphitite burn, the rate of burning depending on the size of the scales and on the purity of the material. L. J. S.

Purification of Commercial Potash and Soda. By Ernst Murmann (*Zeit. anal. Chem.*, 1897, **36**, 379—380).—Potash and soda sold as "purified by alcohol" still contain traces of copper, lead, iron, alumina, and silica. The three former are best removed by cautiously treating the warm solution with hydrogen sulphide. An excess is easily avoided, or it may be afterwards removed by hydrogen peroxide. M. J. S.

Lithium Borate. By Henri L. le Chatelier (*Compt. rend.*, 1897, **124**, 1091—1094).—When boric acid and lithium carbonate are fused together in any proportions whatever, only one borate, Li_2O,B_2O_3, is obtained, and in this respect lithium is analogous to the alkali metals and differs from the metals of the calcium group. The salt crystallises in nacreous, triclinic lamellæ.

In presence of water, boric acid displaces the carbonic anhydride from lithium carbonate, and forms a salt which is analogous to borax, but which is so soluble in water that it could not be isolated.

When the anhydrous borate is dissolved in boiling water and the solution is allowed to cool, the salt, $Li_2O,B_2O_3 + 16H_2O$, is deposited in crystals which belong to the rhombic system; sp. gr. = 1·397 at 14·7°. Its heat of dissolution is $-28·4$ Cal. and the heat of hydration of the anhydrous salt, with formation of the solid hydrated salt, is $+43·4$ Cal. The action of lithium hydroxide (diss.) on boric anhydride (diss.) develops 9·8 Cal. for the first molecule of hydroxide and $9·3 \times 2$ Cals. for two molecules.

The hydrated salt melts completely in its water of crystallisation at 47°, and when heated until it becomes anhydrous there is no evidence of the formation of any intermediate hydrate.

The molecular reduction of the freezing point of the aqueous solutions is 100; the eutectic solution contains 0·6 per cent. of the anhydrous salt, and solidifies at $-0·6°$.

The solubility at first increases slowly with the temperature and then more and more rapidly as the melting point of the hydrated salt is approached. The crystallising point of solutions containing less water than the hydrated salt is 34°. The curve representing the solubility is continuous, but has a vertical tangent at the concentration corresponding with the composition of the hydrated salt, the phenomena being similar to those observed with calcium chloride, many mixtures of fused salts, and metallic alloys.

The crystallised salt effloresces when exposed to air, and absorbs small quantities of carbonic anhydride. C. H. B.

Action of Hydrogen on Solutions of Silver Nitrate: Purification of Hydrogen. By Jean B. Senderens (*Bull. Soc. Chim.*, 1897, [iii], **15**, 991—997).—Conflicting statements by previous investigators have led the author to study the behaviour of aqueous solutions of silver nitrate towards hydrogen. When the purified gas is passed through boiling solutions of the crystallised nitrate, heated in a reflux apparatus, the feebly alkaline action of the liquid is destroyed, and

the quantity of nitric acid produced, the weight of silver precipitated, and the velocity of the action, are found to be proportional to the concentration of the solution; they also increase with the duration of the experiment, but the relation is not in direct proportion, owing to the action of the nitric acid on the metal. Moderately rapid reduction takes place at 80°, the liquid, as in the case of boiling solutions, first becoming turbid and then gradually clear, a grey precipitate of silver being deposited; reduction proceeds still further if the liquid, filtered at this stage, is submitted to the action of the gas. Hydrogen also reduces cold solutions of silver nitrate, change being indicated by separation of metal and by the acidity exhibited by the liquid after treatment with the gas. As in the previous cases, the quantity of acid produced is proportional to the concentration of the solution.

The author's experiments were carried out with electrolytic hydrogen, and also with hydrogen from ordinary sources purified by passage through a concentrated sulphuric acid solution of potassium permanganate, a solution of this salt containing caustic potash, a tube containing cotton wool, a tube containing red-hot copper, and a flask of moderately concentrated silver nitrate. M. O. F.

Alloys of the Silver-Copper Group. By FLORIS OSMOND (*Compt. rend.*, 1897, **124**, 1094—1097).—The researches of various investigators on the melting points of silver-copper alloys indicate that these alloys, after solidification, are simple mixtures of the two metals, the alloy Ag_3Cu_2, described by Levol, being an eutectic mixture. Microscopic examination of a well-annealed button of Levol's alloy, under a sufficiently high power, shows that it is not homogeneous, as Behrens supposed, but has a structure identical with that of the perlite of steels. All other silver-copper alloys except those containing only very small quantities of one of the constituents consist, as the case may be, of yellow crystallites of copper, or white crystallites of silver, more or less completely enveloped in Levol's alloy. Microscopic examination, therefore, confirms the conclusions drawn from determinations of the melting points, and it may be taken that no definite compound Ag_3Cu_2 exists in these alloys. C. H. B.

Silver-Copper Alloys. By FLORIS OSMOND (*Compt. rend.*, 1897, **124**, 1234—1237).—The author has previously shown that alloys of silver and copper contain two constituents which have the appearance of the two metals, but since the properties of the alloys are very far from being the mean of those of their constituents, it would seem that the white and yellow components referred to cannot be simple metals.

Alloys were prepared containing 0·2, 0·5, 1·0, 2·0, and 4·0 per cent. of copper and silver respectively, and when examined quantitatively under the microscope it was found that in both cases part of the metal present in the smaller proportion was not recognisable as a distinct ingredient. Further experiments, in which the alloys were annealed at different temperatures, showed that the appearance of silver is not altered by the addition of 0·2 or 0·5 per cent. of copper, but with 1 per cent. of the latter it becomes recognisable as a separate constituent, and with 2 per cent. it is easily seen. Alloys of copper with

small quantities of silver behave similarly, and the silver becomes visible when the amount of it reaches 0·5 per cent.

These results seem to indicate a mutual solubility of solid copper and silver, as Matthiessen supposed, and this view is supported by the fact that when polished surfaces of silver and copper are placed in contact, and heated at 650—675° in an atmosphere of hydrogen, they adhere somewhat strongly, and the properties of the surface of each metal, after they have been separated, indicates that it contains a small quantity of the other, although the penetration extends only to a minute depth. C. H. B.

Phosphorescent Strontium Sulphide. By José Rodriguez Mourelo (*Compt. rend.*, 1897, **124**, 1024—1026 and 1237—1238).— Strontium sulphide prepared by reducing the pure sulphate with carbon is non-phosphorescent, but when strongly heated with starch it acquires feeble powers of phosphorescence. When prepared in a granular form by heating the commercial carbonate with sulphur, its phosphorescent properties are much more marked, and a still better product is obtained by heating the carbonate at a high temperature in a current of hydrogen sulphide, and afterwards heating the sulphide at very bright redness in an earthen crucible for 4 hours.

Following Verneuil's method for the preparation of calcium sulphide, strontium carbonate was moistened with a dilute solution of sodium carbonate and chloride, dried, converted into oxide, and heated with sulphur and a small quantity of basic bismuth nitrate. The product is much more intensely phosphorescent than any of those described above and the phosphorescence is readily excited.

The following method yields a sulphide which shows an extremely brilliant blue-green phosphorescence even under feeble excitation: 285 grams of ordinary strontium carbonate, 62 grams of flowers of sulphur, 4 grams of crystallised sodium carbonate, 2·5 grams sodium chloride, and 0·4 gram of basic bismuth nitrate are finely powdered and intimately mixed, placed in an earthen crucible, covered with a layer of coarsely powdered starch 2 cm. deep, and heated in a coke fire at bright redness for 5 hours, and allowed to cool during 10 or 12 hours.

As Verneuil has observed in the case of the calcium compound, strontium sulphide loses its power of phosphorescence if finely powdered, but regains it more or less completely if mixed with starch and heated at very bright redness for about 5 hours.

The researches of Verneuil and of the author show that the property of phosphorescence of sulphides of the calcium group is confined to sulphides of the type MS, and is dependent on the presence of small quantities of alkali compounds and of bismuth. Further experiments indicate that in the case of strontium sulphide the presence of a small quantity of sulphate is essential, but if the sulphide is oxidised to any considerable extent its phosphorescent properties disappear.

The strontium sulphide prepared as above contains a small quantity of sulphate, but offers considerable resistance to oxidation, probably owing to the fact that it consists of small rounded grains with a smooth fused surface. It is also but slowly affected by water and even

by dilute acids. It would seem that this structure has considerable influence on the phosphorescent power of the compound.

C. H. B.

Basic Salts of Cadmium. By TASSILLY (*Compt. rend.*, 1897, **124**, 1022—1024).—The salts $CdI_2,CdO,3H_2O$ and $CdBr_2,CdO,3H_2O$ are obtained by heating cadmium oxide in sealed tubes at 200° with a concentrated solution of cadmium iodide or bromide, as the case may be. They are distinctly crystallised, and the crystals act on polarised light. Water has very little action on them, and they are stable in pure dry air at 120°.

When ammonia is added to solutions of cadmium salts, the product is usually a mixture of a basic salt and an ammoniacal salt, but the formation of the latter can be avoided either by strictly limiting the quantity of ammonia, or by using very dilute solutions of both the ammonia and the cadmium salt. In the latter case, the basic salts obtained as precipitates, $CdBr_2,CdO,H_2O$ and CdI_2,CdO,H_2O, are of the same type as the oxychloride described by Habermann; the ammoniacal compounds can be crystallised from the mother liquid and are identical with those obtained by dissolving cadmium salts in ammonia, $CdX_2,2NH_3$. The yield of basic salt is highest with the chloride and lowest with the iodide, whereas the yield of ammoniacal compound follows the reverse order. The basic salts formed by precipitation are decomposed by water.

C. H. B.

Basic Nitrates. By NICOLES ATHANASESCO (*Bull. Soc. Chim.*, 1896, [iii], **15**, 1078—1081. Compare Abstr., 1895, ii, 315).—The basic lead nitrate, $N_2O_5,6PbO,H_2O$, previously described (*Bull. Soc. Chim.*, 1895, [iii], **14**, 175), is also obtained when lead nitrate is left in contact with an excess of aqueous ammonia for a year. When a concentrated solution of zinc nitrate (2 of solid to 1 of water) is heated in sealed tubes for several hours at 310°, the basic nitrate,

$$HNO_3,2ZnO,H_2O,$$

is formed; it crystallises in small, white needles decomposing above 200°, and is insoluble in water, but dissolves in dilute acids. Attempts to prepare the basic nitrate, $Zn(NO_3)_2,7ZnO,4H_2O$, by the incomplete precipitation of zinc nitrate solution with ammonia proved unsuccessful. When a 50 per cent. solution of zinc nitrate is boiled with metallic zinc for about a day, a basic nitrate, $N_2O_5,4ZnO + 4H_2O$, is formed, which crystallises in colourless needles, and loses its water at about 130°.

J. J. S.

Mercury Haloid Double Compounds. By THEODOR HARTH (*Zeit. anorg. Chem.*, 1897, **14**, 323—353).—The present research was undertaken to determine what salts are formed when the following mixtures are dissolved in water: (1) $HgCl_2,2KBr$, (2) $HgBr_2,2KCl$, (3) $HgCl_2,2KCN$, (4) $Hg(CN)_2,2KCl$, (5) $HgBr_2,2KCN$, (6) $Hg(CN)_2,2KBr$; and also how long the reaction takes before equilibrium is established. Solutions of the mercury salts were prepared of about 1 per cent. strength, and the potassium salt solution of such a strength that, on mixing the two solutions in equal volumes, the salts were in the proportions given above; 50 c.c. of the double salt solution

is then extracted with ether, whereby the mercury salt is dissolved and these are then analysed.

With mixtures of mercuric chloride and potassium bromide, and of mercuric bromide with potassium chloride, all the mercury is present as mercuric bromide, both when the solution is extracted 5 minutes after mixing and also after 24 hours. With mixtures of mercuric chloride and potassium cyanide and mercuric cyanide and potassium chloride, and also with the cyanides and bromides, all the mercury is present as mercuric cyanide. In mixtures of mercuric iodide and potassium chloride and mercuric iodide and potassium bromide, all the mercury is present as iodide. In mixtures of mercuric iodide and potassium cyanide, all the mercury is present as cyanide. Double decomposition takes place in all cases in which heat is evolved, and when the heat of formation of the salts, which would be formed by double decomposition, is less than that of the original salts, no double decomposition takes place.

From the above results, it is evident that the products formed by the mixtures $HgCl_2 + 2KBr$ and $HgBr_2 + 2KCl$ are identical; also the products formed by mixing $HgCl_2$ with $2KCN$ and $Hg(CN)_2$ with $2KCl$; as well as the products formed by mixing $HgBr_2$ with $2KCN$ and $Hg(CN)_2$ with $2KBr$.

Determinations of the electric conductivity of the double salts $HgCl_2Br_2K_2$ and $Hg(CN)_2Cl_2K_2$, show that the conductivity is only very slightly higher for the double salt than for potassium chloride, and this behaviour is not in accordance with the constitutional formula $Hg\left.\begin{matrix}Cl_2\\Br_2\end{matrix}\right\}K_2$ assigned to these compounds by Werner.

E. C. R.

Purification of Cerium. By Grégoire Wyrouboff and Auguste V. L. Verneuil (*Compt. rend.*, 1897, **124**, 1230—1233, and Henri Moissan, *ibid.*, 1233).—The difficulty of purifying cerium arises from its tendency to form an intermediate oxide, $Ce_3O_4,3CeO$, in which the mononoxide may be more or less completely replaced by lanthanum, didymium, and other oxides. In order to prevent the formation of this oxide, the oxides obtained by heating the oxalates are dissolved in nitric acid and the solution evaporated to a syrup, diluted until it contains only about 4 per cent. of the oxides, and ammonium nitrate added until the solution contains about 5 per cent. of it. The intermediate oxide is thus completely decomposed and the whole of the oxide, Ce_3O_4, is precipitated in the form of the basic salt, $(Ce_3O_4)_4N_2O_5$. The precipitate is washed with a 5 per cent. solution of ammonium nitrate and is quite free from didymium and lanthanum and the yttrium metals. The cerium in the solution may be recovered by precipitating it as oxalate and repeating the process.

When the oxides contain more than 50 per cent. of cerium, they are not entirely soluble in nitric acid, and in this case the oxalates are dissolved in nitric acid and mixed with hydrogen peroxide and ammonia and boiled, the cerosoceric oxide thus formed being washed and afterwards dissolved in nitric acid.

Any thorium in the cerium oxide is precipitated with the oxide Ce_3O_4,

and consequently the cerium recovered from the mother liquor is free from thorium as well as from the other impurities. In any case, however, it is easy to remove thorium by treating the oxalates, or, better, the nitrates, in neutral solution, with a concentrated solution of ammonium carbonate mixed with ammonia, the last traces being separated by fractional crystallisation of the sulphates, the thorium remaining in the mother liquor. Iron is removed by repeated precipitation with oxalic acid in hot acid solutions ; or by heating the sulphate at 400—450°, when the iron becomes insoluble. Cerium thus purified has constant properties and a constant atomic weight.

According to Moissan, pure cerium can be obtained by preparing the carbide from cerium compounds which show no absorption spectrum, and then fractionally decomposing the carbide with dilute nitric acid. All the iron goes into the first solution ; all the thorium remains in that portion of the carbide which is last attacked. C. H. B.

Compounds of Phosphorus with Iron, Nickel, and Cobalt. By A. Granger (*Bull. Soc. Chim.*, 1896, [iii], **15**, 1086—1089).—Ferric chloride and phosphorus, when separately placed in two small boats and gently heated in a stream of carbonic anhydride, yield ferric phosphide and phosphorus pentachloride. *Ferric phosphide*, Fe_2P_3, which is deposited as small, brilliant, grey needles, is not magnetic and is not attacked by nitric or hydrochloric acid or by aqua regia, but dissolves slowly in potassium hypobromite solution. When raised to a dull red heat, it undergoes no change, but in the blowpipe flame it gives up phosphorus. Nickel and cobalt phosphides may be obtained in a similar manner. *Nickel phosphide* is grey and has a graphitic lustre, it also possesses a strongly marked schistose structure and is very friable. *Cobalt phosphide* is black and can easily be powdered. Both these compounds are less readily acted on by chlorine than is iron phosphide. The *phosphide*, Fe_4P_3, obtained when phosphorus trichloride acts on iron at a moderate heat, crystallises in small, grey prisms ; the same compound is obtained when phosphate of iron is reduced with hydrogen or when metallic iron is heated with phosphorus iodide. The phosphides, Co_2P and Ni_2P, obtained by the action of phosphorus trichloride on cobalt and nickel respectively, are also described. J. J. S.

Constitution of Cobalt, Chromium and Rhodium Bases. By Sofus M. Jörgensen (*Zeit. anorg. Chem.*, 1897, **14**, 404—422).—*Praseo-* and *Violeo-cobalt Salts.*—In a previous paper (Abstr., 1895, ii, 47), the author has shown that the luteo-salts have a symmetrical constitution, as they are the most stable of the cobalt-ammonia-salts. And since the pentamineroseo-salts and the tetramineroseo-salts show a complete analogy with the preceding, they also probably have a symmetrical constitution. The isomeric flavo- and croceo-salts, $(NO_2)_2CoA_4X$, are dinitrotetramine salts of the praseo- and violeo-series ; and the flavo-salts, on account of their near relation to the tetramineroseo-salts, have probably a symmetrical constitution. The praseo-salts, which are so easily obtained from the tetramine-salts, have probably also a symmetrical constitution. Hence it is

probable that the flavo-salts belong to the praseo-series, and the croceo-salts to the violeo-series. The relation between the flavo- and croceo-salts is very different; the former, when treated with hot concentrated hydrochloric acid, loses both its nitro-groups, whereas the latter loses only one. On the other hand, Werner (*Zeit. anorg. Chem.*, 8, 182) has found that praseo-salts, when warmed with sodium nitrite and acetic acid, are converted into croceo-salts. According to Werner's researches, the praseo-tetramine-purpureo-salts are violet; and this is the case with the only known series of these compounds, the chloro-aquotetramine salts. The praseo-chloride, when warmed with dilute hydrochloric acid, is converted into the chloro-aquotetramine chloride, and the green solution of acid dichloropraseo-sulphate soon changes to violet and deposits the chloro-aquotetramine sulphate. Hence the chloro-aquotetramine salts belong to the praseo-series. On the other hand, chloro-aquotetramine chloride is easily prepared by heating carbonato-tetramine chloride with dilute hydrochloric acid, and this reaction takes place in the cold with concentrated acid, whence it follows that the chloro-aquotetramine salts belong to the violeo-series. The formation of flavo-salts from carbonatotetramine-salts and of croceo-salts from praseo-chloride show that they belong to the violeo- and praseo-series respectively. On the other hand, flavo-salts are easily obtained from chloro-aquotetramine chloride, whence it follows that either the chloro-aquotetramine salts belong to the violeo-series, or that the flavo-salts belong to the praseo-series.

The flavo-salts belong, according to Werner, to the violeo-series. However, the flavo-chloride, when allowed to remain in the cold with concentrated hydrochloric acid, is completely converted into chloro-aquotetramine chloride, together with a very small quantity of praseo-chloride. When flavo-nitrate is boiled with dilute hydrochloric acid, it is converted into praseo- and aquo-tetramine salts. Hence the flavo-salts belong to the praseo-series. It is remarkable that the flavo-salts are so easily converted into compounds of the praseo-series, whereas the croceo-salts, which, according to Werner, belong to this series, do not yield chloro-aquotetramine chloride or praseo-chloride when treated with hydrochloric acid.

The diaquotetramine chloride, when warmed at 100° or with hydrochloric acid, is converted into chloro-aquotetramine chloride; the latter yields a red solution with dilute sodium hydroxide, which contains basic diaquotetramine chloride, and when treated with concentrated hydrochloric acid, yields tetramineroseo-chloride. Hence the chloro-aquotetramine salts and the diaquotetramine salts (tetramineroseo-salts) belong to the same series.

The praseo-chloride, when warmed with ammonium carbonate, is converted quantitatively into the carbonatotetramine chloride. Hence the typical violeo-salt belongs to the praseo-series, or the typical praseo-salt to the violeo-series.

The above results show that those differences between the praseo- and violeo-salts which are found in the cobalt ethylenediamine salts are not found in the cobalt-ammonia salts.

The ammonia group can only be arranged in one way as a bivalent radicle, whereas the ethylenediamine group can be arranged in two

ways, that is, $$-\underset{\diagdown C_2H_4 \diagup}{\overset{\diagup C_2H_4 \diagdown}{NH_2\cdot NH_2\cdot NH_2\cdot NH_2}}- \text{ and } -\underset{\diagdown C_2H_4 \diagup}{\overset{\diagup C_2H_4 \diagdown}{NH_2\cdot NH_2\cdot NH_2\cdot NH_2}}-$$
hence it is not necessary, in order to explain this isomerism, to assume that the cobalt atom has different valencies.

Praseo- and Dichro-salts.—The praseo-cobalt sulphate is easily prepared by treating the chloro-aquotetramine chloride (10 grams) with concentrated sulphuric acid (50 c.c.), and allowing the mixture to remain until a violet solution is obtained. The solution is then cooled with ice, and concentrated hydrochloric acid (50 c.c.) gradually added. After 24—28 hours, the green praseo-cobalt salt which crystallises out is washed free from hydrochloric acid with dilute sulphuric acid, and then with absolute alcohol. The yield is very nearly theoretical. If the praseo-salt is washed twice with dilute sulphuric acid in order to extract traces of pentamine salts, and then washed with dilute hydrochloric acid until free from sulphuric acid, a theoretical yield of praseo-cobalt chloride is obtained. Praseo-salts are also obtained pure and in theoretical quantities from diaquotetraminecobalt sulphate, which is easily obtained from carbonatotetraminecobalt sulphate. The diaquotetramine sulphate (10 grams) is dissolved in concentrated sulphuric acid (50 c.c.), allowed to remain 24 hours, then mixed with concentrated hydrochloric acid (50 c.c.), and allowed to remain 48 hours, when the praseo-salt which crystallises out is either washed free from hydrochloric acid by dilute sulphuric acid, or free from sulphuric acid by hydrochloric acid, and the praseo-sulphate or chloride then washed with absolute alcohol. Praseo-cobalt chloride crystallises with $1H_2O$ and is not anhydrous as stated by Klein (*Zeit. anorg. Chem.*, **14**, 28). The bromide, is obtained from the acid sulphate in a similar manner to the chloride. The chlorobromide becomes bright blue if kept at 100° for some 6 weeks; it then loses 25 per cent. in weight, corresponding with a loss of $2NH_3 + Cl$.

The conversion of chloride into sulphate, and of the sulphate into chloride, which takes place so easily in the praseo-salts, also takes place in the dichro-salts. The dichro-chloride, in an analogous manner to the praseo-chloride, yields a dichlorosulphate from which a dichloronitrate can be obtained. The dichro-chloride is obtained by heating the triamine nitrite with concentrated hydrochloric acid.

Acid dichloroaquotriamine cobalt sulphate, $Cl_2Co(NH_3)_3OH_2\cdot SO_4H$, is obtained by treating the dichro-chloride with 50 per cent. sulphuric acid, and after the mixture has remained 24 hours, washing the product free from hydrochloric acid with dilute sulphuric acid; it crystallises in microscopic, greyish-green needles. When treated with hydrochloric acid, it is converted into the dichro-chloride. It dissolves in 5—6 parts of cold water to a greenish solution, which, however, soon changes to violet, and when mixed with hydrochloric acid, yields dichro-cobalt chloride and not the chlorodiaquotriamine chloride. The *silver salt*, $Cl_2Co(NH_3)_3OH_2\cdot SO_4Ag$, is obtained as a bright, olive-green precipitate by treating the compound with silver nitrate. It is easily decomposed by cold water into silver chloride and a blue solution.

Dichloroaquotriamine cobalt nitrate, $Cl_2Co(NH_3)_3OH_2 \cdot NO_3$, is obtained by treating the preceding salt with dilute nitric acid. It crystallises in very small, dichromatic prisms.

Chlorodiaquotriamine cobalt sulphate, $ClOH_2Co(NH_3)_3OH_2 \colon SO_4$, is formed when a cold aqueous solution of the dichro-sulphate is kept. It crystallises in violet-red crusts of rhombic tablets, which are sparingly soluble in cold water, and insoluble in dilute alcohol. When allowed to remain for 24 hours with dilute hydrochloric acid, it is converted into the dichro-chloride. A dilute solution of the dichro-sulphate, after some time, deposits yellow prisms which are probably the triaquotriamine chloride sulphate. E. C. R.

Colloidal Tungstic Acid. By ALEXANDER P. SABANÉEFF (*Zeit. anorg. Chem.*, 1897, **14**, 354—360).—The author has prepared the substance described by Graham (*Proc. Roy. Soc.*, 1864, **13**, 340) as colloidal tungstic acid, and finds that it is an amorphous form of sodium metatungstate. It has the properties ascribed to it by Graham except that the colour of the solution is generally blue, not green; when boiled with dilute acids, it does not give a precipitate, with concentrated acids, however, it yields a yellow precipitate of tungstic hydroxide. The yield amounts to about 20—23 per cent. of the sodium tungstate employed. The author was unable to obtain a product free from alkali either by adding hydrochloric acid during the dialysis or by the action of hydrochloric acid on the colloidal salt. In order to obtain the colloidal salt, it is necessary to employ the sodium tungstate and hydrochloric acid in the proportion $2Na_2WO_4 : 3HCl$, but the reaction proceeds only partially according to the equation $4Na_2WO_4 + 6HCl = Na_2O,4WO_3 + 6NaCl$. A solution of sodium metatungstate and sodium chloride does not behave in the same manner as a solution of the same concentration of sodium tungstate and hydrochloric acid. The latter gives with the excess of acid a precipitate of tungstic hydroxide, whereas the former remains unaltered even on boiling. When the mixture of $4Na_2WO_4$ and $6HCl$ is evaporated on the water bath or at 40°, crystalline sodium paratungstate first separates, then sodium chloride and a double salt of the composition $Na_2O,4WO_3,2NaCl,H_2O$; the mother liquor contains sodium metatungstate, together with a small quantity of sodium chloride.

The crystalline and colloidal modifications of sodium metatungstate have very similar properties. The solutions are neither decomposed nor precipitated by ordinary hydrochloric acid, but the addition of fuming acid causes a precipitation; with alkali, either the para- or the normal salt is formed, according to the proportion added. Both modifications lose the same percentage of water when heated at 100° and 200°, and when heated to redness become insoluble in water. They show an equal molecular conductivity in dilute solutions, but in stronger solutions the molecular conductivity of the colloidal modification is somewhat less. E. C. R.

Thorium. By GERHARD KRÜSS (*Zeit. anorg. Chem.*, 1897, **14**, 361—366).—Thorium hydroxide is most easily prepared by treating solid thorium sulphate with ammonia, taking care to stir the mixture well in order to complete the reaction. The product, which is

a heavy powder easily washed, is boiled with ammonia in order to extract the last traces of sulphate, and then washed with water.

Thorium chloride, $ThCl_4 + 7H_2O$, is obtained by treating thorium hydroxide suspended in absolute alcohol with hydrogen chloride, and allowing the solution thus obtained to crystallise in a vacuum over sodium hydroxide and sulphuric acid. It crystallises in rhombic pyramids, deliquesces in the air, and effloresces when allowed to remain in a desiccator, water and hydrogen chloride being given off. The anhydrous chloride cannot be prepared by heating the crystals in a current of hydrogen chloride or chlorine, as under these conditions a mixture containing oxychloride is obtained. When heated, it decomposes with formation of thorium oxide and evolution of water and hydrogen chloride. It is very easily soluble in water and alcohol, yielding an acid solution, and the addition of ether to the alcoholic solution causes a precipitate of the unaltered salt. When crystallised from alcohol containing water, it separates in slender needles with 11 to 12 H_2O, as described by Cleve.

Thorium Oxychloride.—The preparation of a pure compound of the composition $ThOCl_2$, has not been accomplished; nothing but impure products were obtained by heating the chloride in a current of hydrogen chloride or chlorine, or by heating the hydroxide in a current of hydrogen chloride. The product obtained by heating the crystalline chloride alone always contains more thorium oxide than is required by the above formula. E. C. R.

Constitution of Platosemiamine Compounds. By ALFONSO COSSA (*Zeit. anorg. Chem.*, 1897, **14**, 366—373).—Mainly a criticism of Werner's views on the constitution of the ammonio-platinum compounds.

Mineralogical Chemistry.

Composition and Specific Gravity of Sulfoborite. By KONSTANTIN THADDÉEFF (*Zeits. Kryst. Min.*, 1897, **28**, 264—275).—In the previous analysis of sulfoborite by Naupert and Wense (Abstr., 1893, ii, 325 ; 1895, ii, 276), the determinations of boric acid and water are unsatisfactory. A new examination gives as the mean of five partial analyses :

MgO.	SO_3.	B_2O_3	Fe_2O_3.	Loss on ignition.	Loss at 110—170°.	Insol.	Total.
33·48	22·46	19·79	0·11	23·43	0·10	0·32	99·69

Direct determinations of the water by fusing with sodium and potassium carbonates (Sipöcz's method) gave 20·01 and 19·47 per cent., but as caustic soda may have been formed, these are probably too low. These analyses give the molecular ratios $MgO : SO_3 : B_2O_3 : H_2O =$ 2·98 : 1 : 1·01 : 4·66, and the new formula, $MgSO_4,Mg_2B_2O_5,4\frac{1}{2}H_2O =$ $4MgHBO_3,2MgSO_4,7H_2O$. The molecular ratio of the water is still

unsatisfactory, this being due to the partial decomposition of the material analysed.

As the crystals are acted on by water, the specific gravity determinations were made by weighing the mixture of methylene iodide and benzene in which the crystals floated, or by weighing the crystals with benzene in a pyknometer. Clear fresh crystals gave sp. gr. = 2·440. Unselected crystals gave 2·28—2·445, and the material analysed gave 2·415. L. J. S.

Gersbyite and Munkrudite. By LARS J. IGELSTRÖM (*Zeits. Kryst. Min.*, 1897, **28**, 310—312).—These two "new minerals" occur with "munkforsite" (this vol., ii, 267) in the damourite quartzite at Dicksberg, Sweden. Gersbyite is a blue mineral closely resembling lazulite in appearance; from five analyses, which vary considerably, the formula is given as $3(Fe,Mn,Ca,Mg)O,P_2O_5 + 3(3Al_2O_3,P_2O_5) + 17H_2O$; this is more basic than lazulite.

Munkrudite is a white, transparent, crystallised mineral, which occurs mixed with pyrites; it contains phosphoric acid (about 12 per cent.), sulphuric acid, ferrous oxide, and lime; it is therefore related to svanbergite and "munkforsite," but in outward appearance it is very different from the latter. L. J. S.

[Augite from Montana.] By LOUIS V. PIRSSON (*Zeits. Kryst. Min.*, 1897, **28**, 333; from *Bull. Geol. Soc. Amer.*, 1895, **6**, 389—422. Compare Abstr., 1896, ii, 192).—In a paper by W. H. Weed and L. V. Pirsson on the igneous rocks of the Highwood Mountains of Montana, a description is given of the augite which forms about half of the new rock shonkinite from Square Butte. It occurs as easily isolated, greenish-black crystals over 1 cm. in length, and of the usual habit. Analysis gave:

SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	MgO.	CaO.	Na_2O.	K_2O.	H_2O (at 100°).	Total.
49·42	0·55	4·28	2·86	5·56	0·10	13·58	22·35	1·04	0·38	0·09	100·21

This gives the formula $13Ca(Mg,Fe)Si_2O_6 + 2(Na_2,R'')(Al,Fe)_2SiO_6$.
L. J. S.

Garnet from the Turjinsk mines. By E. VON FEDOROW (*Zeits. Kryst. Min.*, 1896, **28**, 276—290).—The important ore deposits, consisting mainly of copper pyrites, of the Bogoslowsk district in the Urals, occur near the margins of an eruptive mass of augite-garnet rock. The garnets are of two kinds: a dark brown (anal. I), and a pale green which in thin sections is colourless (anal. II). The difference in colour of these garnets is not explained by the chemical composition.

	SiO_2.	Fe_2O_3.	FeO.	CaO.	Al_2O_3.	Mn_2O_3.
I.	34·98	23·77	3·33	34·06	3·32	1·22
II.	38·22	25·62	1·96	31·80	2·11	0·58

The main portion of the paper is occupied by a description of the optical anomalies of the light coloured garnet; the dark coloured is isotropic. L. J. S.

Analysis of a Meteoric Stone which fell at Madrid, February 10th, 1896. By SANTIAGO BONILLA MIRAT (*Bull. Soc. Chim.*, 1897, [iii],

15, 1070).—The analysis of this meteoric stone gave the following results :

SiO_2	MgO.	Fe.	FeS.	Fe_2O_3.	Al_2O_3.	Ni.	CaO.	MnO_2.
58·86	15·95	7·75	7·23	5·11	2·36	1·30	0·51	0·08

Phosphorus, chromium, copper, sodium, potassium, lithium, and nitrogenous compounds, which amounted in all to 0·85 per cent., bring the total to 100.

The sp. gr. = 3·6189 at 15° ; hygroscopic moisture amounted to 0·2841 per cent.

M. O. F.

Chemistry of Vegetable Physiology and Agriculture.

Fatty Matter of Beer Yeast. By ERNEST GÉRARD and P. DAREXY (*J. Pharm.*, 1897, [vi], 5, 275—280).—The authors find that the fatty matter obtained from yeast contains stearic and palmitic acids together with a small quantity of butyric acid. The acids occur to a certain extent as their glyceryl salts, and also probably in the free form. J. J. S.

Formation of "Fruit Ethers" by Yeasts in Green Malt and in Worts. By PAUL LINDNER (*Bied. Centr.*, 1897, 26, 339—340; from *Wochensch. f. Brauerei*, 1896, No. 23, 552).—The intense odour of "fruit-ether" (ethereal salts) observed when green malt is kept, with abundant aëration, is due to a yeast nearly related to *Saccharomyces anomalus*. If the malt is too wet, the yeast production is less, and an odour of sour beet-root is produced. The formation of ethereal salts (probably ethylic acetoacetate) prevents the development of bacteria; and the striking stability of many surface-yeasts is no doubt connected with the sour ethereal odour which they nearly always possess.

In the case of various fruits, such as strawberries, the ethereal salts act as preservatives from putrefaction. *Saccharomyces apiculatus*, and other dextrose yeasts, also give rise to production of ethereal salts, especially under conditions of aëration. Wine loses, perhaps, some of its bouquet when so much pure yeast is added to the must that the *S. apiculatus* is unable to produce ethereal salts. N. H. J. M.

Fixation of Free Nitrogen by the Bacillus of Leguminous Nodules. By MAZÉ (*Ann. Inst. Pasteur*, 1897, 44—54).—The very slight gain of nitrogen hitherto observed in cultivations of the leguminous nodule bacillus is attributed to the fact that nitrogen has only been supplied in the uncombined state, or as ammonia and asparagine, whilst under natural conditions the bacillus has, from the commencement, a store of proteid nitrogen. The amount of hydrocarbon furnished (as in the experiments of Frank, Laurent and Beyerinck) has also been too limited. Moreover, the branched, forked, and flattened forms of the nodules indicate that a sufficient supply of oxygen is of importance.

By cultivating the bacillus on the surface of solid media containing

infusion of haricots, saccharose, sodium chloride, and sodium hydrogen carbonate, very abundant growth was rapidly obtained. The experiments were made in a series of flasks through which air free from combined nitrogen was passed (20 litres per day). The first experiment, which lasted 14 days, showed a gain (in three flasks) of 40·8 milligrams of nitrogen, the initial and final amounts of nitrogen being respectively 62·1 and 102·9 milligrams. Supposing the whole of the sugar present to have been consumed, the relation of nitrogen gained to sugar consumed would be $0·0408 \div 3·075 = 0·013$. Similar results were obtained in a second experiment: nitrogen at commencement = 70·7 milligrams; at conclusion 118·2 milligrams; gain = 47·5 milligrams.

A third experiment was made, employing a liquid instead of a solid medium. The cultures were made in two flasks, each containing 50 c.c. of haricot-broth with sugar (2·6 per cent.), sodium chloride (0·1 per cent.), and a trace of hydrogen sodium carbonate. The experiment lasted 16 days, by which time the whole of the sugar was consumed. The nitrogen fixed amounted to $45·8 - 22·4 = 23·4$ milligrams, and the relation of nitrogen gained to sugar consumed was $0·0234 \div 2·6$.

The results show, therefore, that the bacillus, when cultivated under suitable conditions, readily develops, at the same time exercising its important function of assimilating elementary nitrogen. Symbiosis is not necessary to explain nitrogen fixation, which is effected by the bacillus alone (compare Duclaux, *Ann. Inst. Pasteur*, 1894, 728). The leguminous plant furnishes the bacillus with hydrocarbons and organic nitrogen, thus supplying the organism with the energy necessary to enable it to fix nitrogen.

With regard to the relation of nitrogen fixed to sugar consumed, it is pointed out that the percentages of nitrogen and sugar in sugar-beet are about 0·224 and 14·0. The relation $0·224 \div 14·0 = 0·016$ is rather higher than the relation shown by experiment 3. It is, however, clear that sugar-beet, in its second year, could easily obtain its nitrogen from the air if its accumulated energy could be so utilised. The relation of leaf surface to total weight is at least as great in clover and lucerne as in beet-root, whilst the vegetative period of *Leguminosæ* is longer than that of beet-root. The minimum temperature at which vegetation is manifested is also in favour of the *Leguminosæ*.

N. H. J. M.

Function of Tannin in Plants and especially in Fruits. By C. GERBER (*Compt. rend.*, 1897, **124**, 1106—1109).—In the respiration of soft fruits containing tannin, the volume of the carbonic anhydride evolved is less than that of the oxygen absorbed so long as any tannin remains unaltered. As soon as all the tannin has disappeared, pectin is produced. If the temperature is so low that the cellular activity is not great, the respiration quotient remains lower than unity, but if the temperature is so high that the cellular activity requires more energy than is furnished by the free oxygen, the cellules obtain the necessary energy from the alcoholic fermentation of the sugars, the carbonic anhydride produced by it being added to that produced by respiration, and thus giving a quotient higher than unity. It follows that one of the principal functions of tannins in fruits is to prevent pectic transformations, and thus check the fermentation of the sugars.

Direct experiments with the fruit of *Dyospyros kaki* show that the disappearance of tannins does not involve an increase in the amount of sugar, and experiments on the respiration of *Sterigmatocystis nigra* on a solution of nut-gall tannin lead to the same conclusion. In fruits containing tannins, the latter disappear as the result of complete oxidation, without forming any carbohydrates. C. H. B.

Analysis and Composition of Stick Liquorice. By G. Py (*J. Pharm*, 1897, [vi], **5**, 280—284).—The author has analysed numerous samples of "Spanish liquorice." In each case, the moisture, ash, alcoholic extract, organic substances insoluble in alcohol of 75°, ammonium glycyrrhizate, total nitrogen, and glucose were estimated. Directions are also given for testing for gelatin and gum. J. J. S.

The Carbohydrates of Wheat, Maize, Flour, and Bread. By Winthrop E. Stone (*Office of Expt. Stat. U.S. Agric. Dept. Bul.*, **34**, 1896, 7—28).—The carbohydrates present in grains and in flour were determined, and the changes which take place during the process of bread-making investigated. The analytical methods, which are described, included the separation and estimation of sucrose, invert-sugar, dextrin, starch, pentosans and hemicelluloses, and crude fibre. The process of making the bread is fully described. The following numbers show the percentage amounts of carbohydrates in the dry matter of wheat, maize, flour, and bread:—

		Sucrose.	Invert. sugar.	Dextrin.	Soluble starch.	Normal starch.	Pentosans.	Crude fibre.
Winter wheat	grain...	0·51	0·08	0·27	0·00	30·94	4·54	2·68
	bread...	0·014	0·10	0·68	1·37	27·93	4·16	2·70
Spring wheat	grain...	0·72	0·00	0·41	0·00	30·36	4·37	2·51
	bread...	0·05	0·32	0·23	2·36	27·08	4·34	2·42
Winter wheat	flour...	0·20	0·00	1·06	0·00	34·04	0·00	0·25
	bread...	0·15	0·38	0·91	1·74	31·99	0·00	0·17
Spring wheat	flour...	0·18	0·00	0·90	0·00	46·19	0·00	0·25
	bread...	0·06	0·37	0·27	1·99	39·71	0·00	0·34
Maize	grain...	0·27	0·00	0·32	0·00	42·50	5·14	1·99
	bread...	0·16	0·19	0·00	2·80	40·37	3·54	2·22

Flour made from wheat contains less sucrose and crude fibre than the grain; invert-sugar and pentosans disappear entirely. In making bread, there is a loss of carbohydrates amounting to 1—5 per cent. of the total dry matter; there is a diminution in the amount of sugar, and a tendency to convert the starch into soluble and fermentable forms. This change of starch, however, is confined to the more exposed portions of loaves; in the author's experiments, the amount of starch changed did not average more than 10 per cent. of the total starch.

The temperature of the interior of the loaves baked in the usual manner never exceeded 99°. The loss of weight in "raising" and baking bread amounts to 12—20 per cent., but the actual loss of dry substance is only 3—4 per cent.

All the carbohydrates originally present in flour were found in the bread, and the bread contained, besides, more or less "soluble starch."

N. H. J. M.

Action of Enzymic Ferments on Starches of Different Origin. By Winthrop E. Stone (*Office of Expt. Stat. U.S. Agric. Dept.*

Bul., **34**, 1896, 29—44).—The starches selected for experiment were (1) maize, (2) wheat, (3) rice, (4) potato, and (5) sweet potato (*Batatas edulis*). The enzymes were diastase (from freshly-prepared malt), ptyalin (from human saliva), commercial pancreatin, pancreatin prepared from the pancreas of freshly-killed swine, and "Taka-diastase," the enzyme developed by the fungus *Eurotium oryzæ*.

The results of the experiments show that the different starches vary considerably in their susceptibility to the action of the ferments, some requiring eighty times as long as others for complete solution or saccharification.

Beginning with the starch most readily changed, the relative order is : for malt extract—sweet potato, potato, wheat, and maize ; for saliva —potato, sweet potato, maize, rice, and wheat; for pancreatic fluids —potato, sweet potato, and maize, with wheat and rice unchanged; with "Taka-diastase," potato-starch was the most quickly changed. In some cases, the rapidity of the change is proportional to the concentration of the ferment solution. It is assumed that, in the processes of digestion, the starches would have the same relative susceptibility as they showed in the above experiments. N. H. J. M.

Origin of Silica in Incrustations and Deposits of the Beetroot Sugar Manufacture: Solubility of Calcium Silicate in Saccharine Solutions. By J. WEISBERG (*Bull. Soc. Chim.*, 1896, [iii], **15**, 1097—1100).—The author considers that the greater amount of silica and calcium silicate found in deposits and incrustations of beetroot juice is derived from the lime used in the purification of the juice. The lime obtains its silica, not only from the limestone used, but also from the coke and brickwork of the limekilns. It has been proved that saccharine solutions dissolve calcium silicate more readily than pure water does, and also that the amount of salt dissolved increases with the strength of the saccharine solution. Hot solutions dissolve more calcium silicate than cold, and the presence of carbonic anhydride increases the solubility of lime, and also of calcium silicate in saccharine solutions. In the latter case, part of the calcium silicate is decomposed, yielding calcium carbonate and free silica. It has been found that calcined silica is much less soluble in saccharine solutions than the partially dried compound. J. J. S.

Analyses of Spurrey. By B. BÖGGILD (*Bied. Centr.*, 1897, **26**, 347 ; from *Ugeskrift f. Landmænd*, 1897).—In certain parts of Denmark, the seeds of uncultivated spurrey are collected, ground, and fed, whilst in other parts the plant is cultivated (especially on peaty soils) for the production of hay and seeds. The yield of spurrey hay is about 2000 kilos. per hectare (about 16 cwt. per acre). The following analyses show that the hay is nutritious as compared with average Danish hay, and that the seeds are not so excessively oily as was sometimes supposed :—

	Water.	Crude protein.	Crude fat.	Crude fibre.	N. free extract.	Ash.
Ordinary hay	18·59	7·50	1·54	27·89	38·13	6·35
Spurrey hay	13·71	9·19	2·86	23·75	44·68	5·81
Seeds of *Spergula arvensis vulgaris*	9·85	11·43	8·92	13·87	36·63	19·30
Seeds of *S. Maxima*	12·15	13·06	9·56	8·63	53·60	3·00

N. H. J. M.

Soils of Cameroon, Senegambia, and German East Africa: Improved Method of Soil Analysis. By FERDINAND WOHLTMANN and H. KRATZ (*Bied. Centr.*, 1897, **26**, 292—296; from *J. Landw.*, 1896, 211).—The mineral food-constituents present in soil are extracted by macerating the soil (450 grams) for 48 hours with cold hydrochloric acid (sp. gr. = 1·15; 1500 c.c.). In the case of soil containing much iron and alumina (25—30 per cent.), twice as much hydrochloric acid is employed. The single constituents are estimated, as a rule, by the ordinary methods. Silica is estimated as usual by evaporating down, &c., but in soils containing much iron and alumina, about 10 grams of sodium chloride is added to the solution to prevent the production of insoluble compounds. Lemmermann points out that the addition of sodium chloride is unnecessary, as the insolubility produced in presence of iron and alumina refers only to water; moderate heating after moistening with strong hydrochloric acid will always render the compounds soluble. N. H. J. M.

The Function of Humic Substances in the Fertility of Soils. By ARMAND GAUTIER (*Compt. rend.*, 1897, **124**, 1205—1206).—According to the author's view, the chief function of the humic substances in the soil is to afford nutriment for the algæ and microbes which have the power of fixing atmospheric nitrogen. In the absence of such nutriment, the algæ and microbes are more or less starved, and their activity in fixing nitrogen is thereby greatly reduced, with the result that the soil remains comparatively unfertile. C. H. B.

Analytical Chemistry.

Apparatus for the Industrial Analysis of Gases. By LÉO VIGNON (*Compt. rend.*, 1897, **124**, 1244—1246).—This apparatus consists of a horizontal tube closed at one end by a stopcock, whilst the other end terminates in a vertical explosion vessel, fitted at its upper end with a stopcock, and at its lower with a movable mercury reservoir. Between the extremities of the horizontal tube there are attached to it by means of vertical side tubes fitted with stopcocks (1) a vertical measuring tube, which is at the end of the horizontal tube furthest away from the explosion tube. This tube is attached at its lower end to a movable mercury reservoir, and is surrounded by a water jacket. (2) One, two, or more cylindrical bulbs containing the necessary absorption reagents. These pipettes have vertical stems below the bulbs as well as above, and their lower ends dip into the reagents contained in Woulff's bottles. The gas is passed from one tube or bulb to another by means of the movable mercury reservoir.

C. H. B.

Separation of Tellurium from Antimony. By WILHELM MUTHMANN and E. SCHRÖDER (*Zeit. anorg. Chem.*, 1897, **14**, 432—436). —The method is based on the decomposition of tellurium sulphide and

the insolubility of the resulting tellurium in somewhat concentrated hydrochloric acid.

The solution of the two metals in hydrochloric acid is mixed with tartaric acid, and completely precipitated with hydrogen sulphide; the precipitate is separated and washed, and digested with a warm solution of potassium sulphide, whereby all the tellurium is dissolved. This solution, which should not contain a large excess of potassium sulphide, is gradually added to a solution containing 20 per cent. hydrogen chloride and some tartaric acid, and digested until the precipitate becomes flocculent. The precipitate, which consists of a mixture of tellurium and sulphur, is separated and washed with hot hydrochloric acid, and then with water containing tartaric acid until quite free from antimony. The antimony is then determined in the filtrate by any of the ordinary methods. The precipitate of tellurium and sulphur is dissolved in fuming nitric acid, and the tellurium weighed either as metal or dioxide. The results are accurate.

An analysis of "Blättererze," from Nagyág, by this method gave the following results: Pb, 53·55; Au, 9·47; Sb, 6·05; Te, 18·99; S, 11·895; quartz, 0·56 per cent., which corresponds to the empirical formula $Pb_{10}Au_2Sb_2Te_6S_{15}$. E. C. R.

Extremely Sensitive Reagent for Detection and Colorimetric Estimation of Nitrous Acid. By E. RIEGLER (*Zeit. anal. Chem.*, 1897, **36**, 377—378).—The author has prepared a reagent which is twenty times as sensitive as the 1 : 4-naphthylaminesulphonic acid previously recommended (this vol., ii, 230). A solution is made of 2 grams of chemically pure sodium 1 : 4-naphthylaminesulphonate and 1 gram of β-naphthol (puriss.) in 200 c.c. and filtered. The solution is colourless, but has a violet-blue fluorescence. It may be preserved unchanged in the dark. It is even better to mix the dry substances intimately in a mortar and preserve the dry mixture, adding a few centigrams of it to the liquid to be tested. Both for qualitative and quantitative tests, the operations are the same as with naphthylaminesulphonic acid (pp. 230, 385), except that the type solution of nitrite should be $\frac{1}{10}$th the strength there recommended, since this reagent is capable of detecting 1 part and estimating 5 parts of N_2O_3 in 100 millions of water. M. J. S.

Combustion Boat with Partitions. By ERNST MURMANN (*Zeit. anal. Chem.*, 1897, **36**, 380, 381).—Substances which fuse when heated are liable to flow to the cooler end of the ordinary boat, and, when reached by the heat, to decompose too rapidly for accurate work. By dividing the boat into compartments, this difficulty is entirely obviated. M. J. S.

Precipitation of Zinc as Sulphide. By JEAN MEUNIER (*Compt. rend.*, 1897, **124**, 1151—1152).—The difficulty usually experienced in obtaining zinc sulphide in a form that is readily filtered and washed arises from the use of an excess of the precipitant. The solution should be carefully mixed with ammonia until the precipitate is just redissolved. A slow current of hydrogen sulphide is passed into the liquid, but is discontinued as soon as precipitation is complete, this

point being ascertained by testing a few drops of the liquid on a white plate with a drop of ferrous sulphate solution. The precipitate settles rapidly, and is readily filtered and washed, the operations being more rapid if the liquid is warm. The precipitation is not interfered with by relatively large quantities of ammonium salts.

C. H. B.

Employment of Ammonium Carbonate in Water Analysis. By ADELBERT RÖSSING (*Zeit. anal. Chem.*, 1897, **36**, 359—369).—The well-known discordance generally observed in the estimation of the total fixed mineral constituents of natural waters, between the results of evaporation and ignition on the one hand, and of estimation of the individual bases and acid radicles on the other, and the disputed question of the effect on this discordance of the ammonium carbonate used by some analysts for recarbonating the alkaline earths causticised by the ignition, induced the author to examine the behaviour of such salts as commonly occur in waters, when evaporated and ignited with ammonium carbonate. Potassium and sodium chloride and sodium sulphate did not alter in weight when repeatedly treated with ammonium carbonate. Calcium and magnesium sulphates both exhibited a considerable loss of sulphuric acid with corresponding decrease in weight. This loss increases on successive treatments, so that the attainment of a constant weight would mislead to a greater extent than the acceptance of the first weighing. The use of an aqueous solution of carbonic anhydride for recarbonating the alkaline earths seems free from error as far as the above-named salts are concerned. When applied, however, to residues containing magnesia, it fails to restore the whole of the lost carbonic anhydride. Mohr's proposal to add a known weight of sodium carbonate to waters containing magnesium chloride fails, therefore, to attain the desired result. The recommendation of Fresenius to convert the whole of the bases into sulphates by evaporation with an excess of sulphuric acid would seem open to a similar objection, since it is necessary to ignite the residue with ammonium carbonate in order to convert the alkali hydrogen sulphates into normal sulphates. Direct experiments show, however, that the loss of sulphuric acid from calcium and magnesium sulphates when solid ammonium carbonate is used is comparatively small, and, for the purposes of water analysis, may be neglected. M. J. S.

Iodimetric Estimation of Sugars. By GYSBERT ROMIJN (*Zeit. anal. Chem.*, 1897, **36**, 349—359).—Glucose is oxidised by iodine, in presence of alkali, to gluconic acid with approximate completeness, but if excess of alkali hydroxide is employed the oxidation is too irregular to form the basis of an analytical process. By using borax as the alkali, the reaction, under definite conditions of time, temperature, and dilution, becomes sufficiently regular. The iodine solution recommended contains 40 grams of borax and about 10 grams of iodine per litre. Of this solution, 25 c.c. is mixed with 25 c.c. of the sugar solution containing about 0·15 gram of sugar, in a narrow-necked flask with long glass stopper. The stopper is wired down, and a few drops of water placed in the gutter formed by the stopper and the neck of the flask. The flask is then kept, by means of a thermostat, at 25° for 16—22 hours,

after which the contents are acidified by hydrochloric acid, and the unabsorbed iodine titrated by thiosulphate. For 2 atoms of iodine, 1 molecule of sugar ($C_6H_{12}O_6$) is calculated, and, with glucose, results ranging from 98·6 to 100·9 per cent. were obtained. At greater dilutions, the results were higher, owing to the hydrolytic dissociation of the borax. Very similar results were obtained with the aldoses, galactose, mannose, arabinose, xylose, and rhamnose, whilst levulose, and the ketoses in general, were scarcely attacked, so that the process serves for estimating a sugar of the former class in presence of one of the latter. Sorbose behaves like the ketoses. Maltose, and especially lactose, consume more iodine than dextrose. Saccharose, raffinose, and stachyose, which do not reduce Fehling's solution, are oxidised to a considerable extent by the borax-iodine solution. The process is not applicable to the estimation of sugar in wine or urine, since iodine is consumed by glycerol and by uric acid, as well as by many other substances, such as mannitol, lactic acid, &c. M. J. S.

Volumetric Estimation of Acetone. By EDWARD R. SQUIBB. (*J. Amer. Chem. Soc.*, 1896, **18**, 1068—1079).—The process used by the author is a slight modification of the well-known method of Robineau and Rollin, which is based upon the titration of acetone by means of potassium iodide and sodium hypochlorite in an alkaline solution.

The following reagents are required: *A standard solution of acetone.* 50 c.c. of water is put into a flask of 100 c.c. capacity, and carefully weighed; 13 c.c. of pure acetone is added, and the whole is again weighed. The liquid is now transferred to a graduated measuring flask, the weighing flask being well rinsed, and then diluted, so that 10 c.c. contains 0·1 gram of acetone. The author advises keeping this solution in the dark.

Potassium iodide.—250 grams of the salt is dissolved in water, and the solution made up to a litre; each c.c. will contain 2·5 grams of the iodide.

Sodium hydroxide.—257 grams of commercially pure soda is dissolved in water and the solution made up to 1 litre. When quite clear, 850 c.c. of the solution is poured off and added to the solution of potassium iodide, making 1850 c.c. of total solution.

Sodium hypochlorite.—One litre of *liquor sodæ chloratæ*, U.S.P. (containing 2·6 per cent. of available chlorine) is mixed with 25 c.c. of the sodium hydroxide solution.

Bicarbonated starch solution.—0·125 gram of starch is ground up with 5 c.c. of cold water, added to 20 c.c. of hot water, and boiled. When cold, 2 grams of sodium hydrogen carbonate is added and stirred until dissolved. This preparation will keep for three months, or longer.

The titration.—Ten c.c. of the dilute acetone is put into a 50 c.c. beaker, and 20 c.c. of the mixed soda and potassium iodide solution added; into this, the hypochlorite is rapidly run in from a burette until 8 or 10 c.c. has been added. The iodoform is then allowed to settle, and a few drops more of the hypochlorite added. Should this produce a dense cloudiness, a little more is added, until finally the cloudiness is only very slight. It is then tested by starch, a drop of the

starch solution being placed near to a drop of the liquid on a white porcelain plate, and the two drops run into one another. If no blue colour is visible, a few more tenths of a c.c. of hypochlorite solution is run in, repeating the process until the starch gives a blue coloration. Having now checked the standard solution, any number of acetone estimations may be made, but it must be remembered that the hypochlorite does not keep, and must, therefore, be standardised daily. It is also advisable, when dealing with acetone solutions of unknown strength, that the estimation should be repeated, taking such a quantity of solution that the amount of acetone is about the same as that used in the check experiment.

The author also confirms the statement that the presence of ethylic alcohol does not interfere with this process, although it is an iodoform yielding substance. L. DE K.

Estimation of Acetone in Urine. By G. ARGENSON (*Bull. Soc. Chim.*, 1897, [iii], 15, 1055—1058).—Léoben's method of determining acetone in urine consists in distilling the liquid until a fourth part has passed over, converting the acetone into iodoform, decomposing the latter with alcoholic potash, and determining the potassium iodide by means of a standard solution of silver nitrate. Numerous experiments having shown that the quantity of iodoform produced is invariably smaller than that required by the equation

$$COMe_2 + 3I_2 + 4KOH = CHI_3 + CH_3{\cdot}COOK + 3KI + 3H_2O,$$

and depends largely, moreover, on experimental conditions, the author has elaborated a table which supplies the weight of acetone per litre, corresponding with the volume of silver nitrate employed. The conditions for which this table holds good are clearly laid down.

M. O. F.

Extension of Legal's Reaction to Compounds containing the Acetyl Group, and their Derivatives. By GEORGES DENIGÈS (*Bull. Soc. Chim.*, 1897, [iii], 15, 1058—1064).—Legal's test for acetone consists in adding to the liquid a few drops of a solution of sodium nitroprusside, followed by a caustic alkali; a red coloration is produced, and gradually diminishes, but deepens to carmine on treatment with excess of glacial acetic acid.

The author has made the following generalisations concerning this change. (1) All those compounds which give Legal's reaction contain the acetic group, the carbonyl radicle being combined with either hydrogen or a hydrocarbon residue. (2) Compounds containing an acetyl or substituted acetyl complex do not give Legal's reaction if the carbonyl radicle is united to the groups OH, OR, OM (acetates), NH_2, or to chlorine, these substances developing, on the other hand, a red coloration with ferric chloride. (3) Those compounds which contain an acetyl group of which the carbonyl radicle is combined with an aromatic hydrocarbon give rise to a blue coloration when submitted to Legal's test.

Acetylphenylhydrazine, and hydrazine derivatives generally, must be excluded from the second of the above generalisations. These substances do give Legal's reaction, but the coloration produced differs from the ordinary one in being transformed into violet by hydrochloric acid instead of being destroyed. M. O. F.

Colour Reactions of the Aldehydes and Ketones. By BÉLA VON BITTÓ (*Zeit. anal. Chem.*, 1897, **36**, 369—376).—Compounds of the aldehyde or ketone class, in which the formyl or carbonyl group is not combined with a completely substituted hydrocarbon, give, with salts of the metadiamines, either immediately or in the course of an hour or two, deeply coloured solutions with intense green fluorescence. Ortho- and para-diamines also give colour reactions, but without any marked fluorescence. To obtain the reaction, a few c.c. of a 0·5—1 per cent. solution of the metadiamine hydrochloride is added to the aqueous or alcoholic solution of the substance to be tested. Alkalis destroy the colour, which returns on acidifying. Mineral acids, with the exception of metaphosphoric acid, enfeeble the colour. The reaction occurs with aromatic aldehydes, whether the formyl is united directly with a benzene residue or through the intermediary of a fatty alkyl. The reaction is not exhibited by the mixed ketones or by the ketonic acids. The colour produced is in most cases yellow to orange, but cinnamaldehyde gives a cherry-red, and diethyl ketone a violet-red.

The author has also studied the behaviour of Schiff's reagent (a 0·025 per cent. solution of magenta decolorised by passing sulphurous anhydride through it (compare this vol., ii, 235) with a number of aldehydes and ketones. The violet colour is produced by all the aldehydes of the fatty series, and by fatty ketones in which the carbonyl is united with at least one methyl group. It is not produced either by monochloracetone or by diethyl ketone, or by the mixed ketones or ketonic acids. Cinnamaldehyde, and similar compounds, give a yellow coloration, subsequently passing into violet. Schiff's reagent, when boiled and cooled, always acquires a bluish-violet colour, which unfits it for the above reactions. It ought, therefore, never to be heated. M. J. S.

Analysis of Wheat. By AIMÉ GIRARD (*Compt. rend.*, 1897, **124**, 876—882, 926—932).—See this vol., ii, 382 and 425.

Hæmochromogen as a Test for Blood. By ZAKARIÁS DONOGÁNY (*Virchow's Archiv*, 1897, **148**, 234—235).—The most delicate test, of those investigated, for the purpose of detecting blood in urine, fæces, sputum, &c., is the preparation of hæmochromogen crystals, and the spectroscopic examination of the orange-red solution which they form. These are best obtained by adding pyridine to the suspected fluid, previously rendered alkaline with ammonium sulphide, or, better, with sodium hydroxide. W. D. H.

The Uncertainty of the Guaiacum Reaction for Active Diastase. By BRONISLAW PAWLEWSKI (*Ber.*, 1897, **30**, 1313—1314).—The author considers the guaiacum reaction to be very uncertain; not only does this reagent give a similar colour with peptone, gelatin, albumin, &c., but even on addition of hydrogen peroxide to the tincture a blue colour is produced. The test is much better suited for the detection of nitrous acid, a deep blue coloration being instantly formed in solutions containing as little as 0·00005 gram of a nitrite.

J. F. T.

General and Physical Chemistry.

Examination of some Spectra. By PAUL ÉMILE LECOQ DE BOISBAUDRAN (*Compt. rend.*, 1897, **124**, 1419—1421).—The author replies to certain criticisms of Eder and Valenta on his description of the spectra of gold and gold chloride, and maintains the accuracy of his former statements. C. H. B.

Iron Lines present in the Hottest Stars. By JOSEPH NORMAN LOCKYER (*Proc. Roy. Soc.*, 1897, **60**, 475—476).—On a former occasion, the author observed that in the case of iron, two lines in the visible spectrum at 4924·1 and 5018·6 on Rowland's scale, were greatly enhanced in brightness on passing from the arc to the spark. Seven additional lines have been found whose brightness is enhanced at the highest temperature. It appears probable that, in a space heated to the temperature of the hottest spark, and shielded from a lower temperature, these lines would constitute the spectrum of iron. In the hottest stars, iron is practically represented by the enhanced lines alone; those which build up, for the most part, the arc spectrum are almost or entirely absent. But the enhanced lines may be absent from the spectrum of a star, either on account of too low or too high a temperature. In the case of low temperature, iron is represented among the lines in the spectrum, but at the highest temperature all visible indications of its presence seem to have vanished. H. C.

Absorption of Ultra-violet Rays by Gases and Liquids. By J. PAUER (*Ann. Phys. Chem.*, 1897, [ii], **61**, 363—379).—Compare this vol., ii, 393.

Colour of the Phosphorescence of Strontium Sulphide. By JOSÊ RODRIGUEZ MOURELO (*Compt. rend.*, 1897, **124**, 1521—1523).—The colour of the phosphorescence of strontium sulphide is always bluish-green, the hue being most nearly pure green when the sulphide has been prepared by the author's modification of Verneuil's method (this vol., ii, 450). The intensity of the phosphorescence depends on the composition and physical condition of the sulphide, and is not directly affected either by the temperature at which it is heated or by the duration of the heating. It is noteworthy that the most intensely fluorescent variety need not be heated more than three hours, and that an excessively high temperature is not necessary. Nothing is gained by prolonging the heating for several hours beyond the time necessary to gain the maximum effect either with this variety or with those prepared in other ways. C. H. B.

Behaviour of Minerals with the X-Rays. By CORNELIUS DOELTER (*Jahrb. f. Min.*, 1897, i, 256—257. Compare this vol., ii, 45). —Using the methods previously described, the transparency of some more minerals for the Röntgen X-rays are compared. Phenakite is one of the most transparent of minerals, and is placed in the author's

group II. Olivine, tourmaline, biotite, zoisite, and sphene have about the same transparency as calcite (Group VI.). Sapphire seems to be more transparent than ruby, and aquamarine is more transparent than the darker coloured emerald. L. J. S.

Refractive Powers of Mixtures of Two Liquids. By F. ZECCHINI (*Gazzetta*, 1897, **27**, i, 358—383).—The author has examined the relation between the refractive power and the density of mixtures of ethylic alcohol and carbon bisulphide, ethylic alcohol and α-bromonaphthalene, ethylic alcohol and cinnamaldehyde, phenylic thiocyanate and carbon bisulphide, cinnamaldehyde and carbon bisulphide, α-bromonaphthalene and carbon bisulphide, and of anethoil and carbon bisulphide, in a similar manner to Pulfrich (*Zeit. physikal. Chem.*, **4**, 562), and Buchkremer (Abstr., 1891, 2). Using the nomenclature adopted by the latter, the author writes the equations $(N - N_v)/N = a(D - D_v)/D$ and $(D - D_v)/D = c$ in the form $N_v(1 - ac)(p_1 + p_2) \div D(1 - c) = N_1p_1/d_1 + N_2p_2/d_2$ in which v_1 is the volume of one of the constituent liquids of density $d_1 = p_1/v_1$, and refractive index N_1 whilst v_2 is the volume of the other constituent liquid of density $d_2 = p_2/v_2$ and refractive index N_2; when $a = 1$ or $c = o$, the equation becomes $N(p_1 + p_2)/D = N_1p_1/d_1 + N_2p_2/d_2$.

The author fully confirms the conclusions of Pulfrich and of Buchkremer (*loc. cit.*), and notes that when the value $(1 - ac)/(1 - c)$ differs little from unity, the rule cannot be experimentally verified.

W. J. P.

Use of Aldehydes and Ketones in the Presence of Sodium Sulphite for Developing the Latent Photographic Image. By AUGUSTE LUMIÈRE, LOUIS LUMIÈRE, and ALPHONSE SEYEWETZ (*Bull. Soc. Chim.*, 1896, [iii], **15**, 1164—1169).—It is well known that formaldehyde, when added to an organic developer, considerably increases the reducing power of the developer; and the authors show that other aldehydes and also ketones exhibit the same property. The aldehyde or ketone, however, will not act by itself, but requires the presence of sodium sulphite; the sulphite cannot be replaced by other alkali salts such as sodium acetate or phosphate. The same compounds not only accelerate development but, in the presence of sodium sulphite and a phenolic developer, also bring out the latent image without the use of alkali. The authors suppose that in the presence of the phenolic developer the sodium sulphite is, to some extent, decomposed into free alkali which combines with the phenol and into sodium hydrogen sulphite which combines with the aldehyde or ketone. This view is supported by experimental results.

It is found that the best results are given by pyrogallol, sodium sulphite, water, and acetone. The best developing mixture in the case of quinol is water (100 grams), quinol (3 grams), sodium sulphite (10 grams), and acetone (10 c.c.). J. J. S.

Photo-electric Phenomena and Photographic Processes. By H. LUGGIN (*Zeit. physikal. Chem.*, 1897, **23**, 577—635).—The author exposed to light a sensitive electrode similar to that previously described (Abstr., 1894, ii, 405), but which could be raised to any

definite potential above that of the liquid. The current produced or the photo-current was measured, and it was found that an intimate connection exists between the strength of the photo-current and the depth of the darkening of the sensitive electrode. As the potential of the electrode is increased, however, the photo-current decreases, and ultimately a potential is reached where the current becomes zero and by increased exposure may pass over to a current of opposite sign. Where the action of the current is to remove the halogen and hence cause darkening of the electrode, the current is called normal or positive, currents which act in the reverse sense being known as *solarisation current*, and experiments show that both kinds of current may be produced with the same electrode, according to its potential and the light intensity. The solarisation current, in the case of silver chloride electrodes, more readily occurs with yellow light, whilst, on the other hand, blue light favours the production of the normal current, which, in contradistinction to the solarisation current, is coterminous with the exposure. The potential at which no normal current is produced is known as the equilibrium potential, and a linear equation is found to hold for the relation of the photo-current to the defect from the equilibrium potential, and in the equation the constant is probably dependent on the dissociation of the silver salt. The author endeavours to connect these results with the purely photographic phenomena, and considers that solarisation appearances are intimately and causally connected with the solarisation current, and at any rate with printing out papers the connection between the photo-electric and photographic phenomena is in the author's opinion established. The applicability of the halogen salts appears also to be connected with the value of the equilibrium potential, and the author finally discusses at some length the production of images by development. L. M. J.

Thermal Conductivity and Ion Motion. By GEORG BREDIG (*Zeit. physikal. Chem.*, 1897, **23**, 545—546).—Jäger has shown that the thermal conductivity of a salt solution is given by the expression $k = k'(1 - ap)$ where k' is the conductivity of water, p the percentage of salt in the solution, and a, a specific constant. By making $k' = 100$ and $p = 100$ the expression $k = 100 - a10^4$ is obtained, and if this is multiplied by the equivalent weight, the result is what the author terms the equivalent conductivity. Jäger's numbers are employed, and show that, like the electrical conductivity, this constant also is an additive property of the ions. L. M. J.

Distribution of a Current among the Ions in a Solution. By ED. V. STACKELBERG (*Zeit. physikal. Chem.*, 1897, **23**, 493—496).—In the case of a solution containing many ions, the author deduces for (1) the total current, and (2) the portion conveyed by each set of ions the expressions:—(1), $E = C(N_a u_a + N_b u_b + \ . \ . \ . \ N_m u_m + \ . \ . \ . \ )$ and (2) $\Delta N_a = E \cdot N_a u_a / \Sigma(Nu)$, where N_a, &c., . . . are the number of gram equivalents of the free kations, N_m . . . the number of gram equivalents of the anions, and u_a . . . their respective migration velocities.

L. M. J.

Electrolytic Dissociation in Acetone Solution. By GIACOMO CARRARA (*Gazzetta*, 1897, i, 207—222).—The author notes that

Zelinsky and Krapiwin (this vol., ii, 5) have ignored his previous work (Abstr., 1896, ii, 511) on electrolytic dissociation in methylic alcohol solution, and claims priority as against Laszczynski (*Zeit. f. Elektrotec. u. Elektrochem.*, 1895, 55), certain of the results arrived at by the latter having been previously deduced by the author (Abstr., 1894, ii, 310; 1895, ii, 302).

Using a carefully purified sample of acetone, boiling at 56·3° under 761·4 mm. pressure, and having a conductivity of $\mu = 0·00066$ to 0·0010 at 25°, the author has determined the electrical conductivity of solutions of various electrolytes in acetone solution; the values obtained are

Electrolyte.	Acetone.		Water.	Methylic Alcohol.
	v	μ_v	μ_∞	μ_∞
LiCl	1024	33·42	110	77·3
KI	2048	153·6	142·6	97·63
NaI	1024	139·85	121·4	89·77
NH_4I	∞	152·5	142·6	105·25
NMe_4I	2692	119·76	115·6	115·3
NEt_4I	2048	111·04	199·2	91·13
SMe_3I	2048	117·49	119·3	119·68
SEt_3I	∞	167	107·6	112·53
HCl	63·55	2·21	395·2	133·08
$CCl_3·COOH$	46·48	0·419	358	121·48

summarised in the accompanying table, those given previously (Abstr., 1806, ii, 511) for aqueous and methylic alcohol solutions being also quoted to assist comparison.

Potassium and sodium iodides are the only salts used of which the molecular conductivities in acetone solution change on dilution in such a way as to approximate to a limiting value; with ammonium iodide, there seems a tendency for the conductivity to change normally with dilution, but for the other electrolytes examined the increase of molecular conductivity, which attends a doubling of the volume, increases, instead of decreasing, as the dilution increases. This kind of behaviour has also been observed by Laszczynski (*loc. cit.*) with acetone solutions of mercuric chloride, silver nitrate, and sodium thiocyanate. It is noteworthy that hydrogen chloride, trichloracetic acid, and lithium chloride, hygroscopic substances, although highly dissociated in aqueous solution, give very low electrical conductivities in acetone; the low values may be due, in the case of lithium chloride, to combination with the solvent. The electrical conductivity of a solution depends (*a*) on the dissociating power of the solvent and (*b*) on the "electrolytic friction" or friction between the solvent and the ions. These two factors seem, in the case of aqueous solutions, to operate in the same direction on the molecular conductivity, that is to say, whilst the actual dissociating power is great, the friction is small. In acetone solutions, however, the solvent seems to possess but slight dissociating power, and at the same time interposes but slight electrolytic friction,

so that the velocity of ionic migration is great. The small dissociating power of acetone is well shown by comparing the number of litres (n) in which a given quantity of an electrolyte must be dissolved in order that the degree of dissociation (d) shall be the same in the various solvents dealt with. Thus, when d is 0·760 for triethylsulphine iodide, n is 8 with water as the solvent, 39 with methylic alcohol, 504 with ethylic alcohol, 1015 with propylic alcohol, 89 with allylic alcohol, and 498 with acetone. Again, when d is 0·920 for potassium iodide, n is 24 for water as the solvent, 436 for methylic alcohol, and 512 for acetone.

W. J. P.

Electrolytic Dissociation of Methylic Alcohol and of Water dissolved in it. By GIACOMO CARRARA (*Gazzetta*, 1897, **27**, i, 422—440. Compare Abstr., 1896, ii, 511).—The author carefully purified methylic alcohol by dehydration with copper sulphate and barium oxide, subsequently distilled it from a few pellets of sodium, and then distilled it under 20 mm. pressure from 2 per cent. of phosphoric anhydride. The electrical conductivity of the sample thus obtained was determined by Kohlrausch's method, the alcohol being distilled into the flask containing the electrodes; a large number of determinations were made under various conditions, and as the end result the author states the electrical conductivity of methylic alcohol to be $0·072 \times 10^{-10}$ at 25°, a much smaller value than that given by Völlmer (*Ann. Phys. Chem.*, **52**, 348), namely $1·22 \times 10^{-10}$, which is the smallest value previously recorded.

It is concluded that methylic alcohol is partially dissociated and about twice as much so as water; 1 gram-molecule of methylic alcohol is dissociated in about 5·5 million litres at 25°. The electrical conductivity of methylic alcohol is not affected by the addition of 0·23 per cent. of benzene, but falls to about two-thirds on adding 0·71 per cent. of benzene; the electrical conductivity of the alcohol is thus due to the presence of an electrolyte which, in accordance with the general rule, has a lower conductivity in a mixture of solvents.

It is further shown that water is dissociated in methylic alcohol solution, and in very dilute solutions the ionic concentration is proportional to the square root of the total concentration of the water. In very dilute solutions, the dissociation of the water is always rather greater than the electrolytic dissociation of water in aqueous solution; that dilute solutions of water in ethylic alcohol show the contrary effect to this is probably due to the much less considerable dissociating power of ethylic alcohol.

W. J. P.

The Chemical Action of Electrical Oscillations. II. By ALEXANDER DE HEMPTINNE (*Zeit. physikal. Chem.*, 1897, **23**, 483—492).—In order to ascertain the effect of the wave-length, the author determined the maximum pressure at which the tube became luminous when subjected to the influence of the oscillation, investigating the cases of tubes with allylic alcohol, acetone, propylic aldehyde, methylic alcohol, and ethylic alcohol. Of these, the two last showed a marked increase of sensitiveness as the wave-length increased, but, in the other cases, the pressure remained almost constant except for acetone, where a maximum of sensitiveness was obtained in the middle of the series.

The author describes an experiment illustrating the metallic conductivity of a glowing tube, and points out that from the analogy to metals, the chemical action would be expected to vary with the wave-length. According to Ebert, the spectra of vapours vary with the wave-length, but, although the author also finds a slight variation in the compounds examined, he points out that this may be due to decomposition and the formation of new products; the influence on the spectrum of the substance itself, therefore, is doubtful. In general, the sensitiveness increases with the molecular weight, but it is dependent also on other data, thus ethylic ether is less sensitive than acetone. Temperature has also a marked effect, but its complete investigation was postponed; a magnetic field appeared to have no influence. L. M. J.

Variation with Temperature of the Transference Ratios of Cadmium in Aqueous Solutions. By VICTOR GORDON (*Zeit. physikal. Chem.*, 1897, **23**, 469—482).—The electromotive force of the element $-Cd \mid CdSO_4aq. \mid \mid CuSO_4aq. \mid Cu-$ increases with temperature, indicating a diminution in the concentration of the cadmium ions, which may be due to the formation of molecular aggregates, these having been proved to exist in the case of the halogen cadmium salts. On this assumption, the transference ratio should not be greater at high than at low temperatures; the author determined this value at different temperatures, that is, the ratio of the weight of cadmium which has actually passed from the anode liquid, to the quantity deposited on the cathode, or dissolved from the anode. The values obtained were (1) 11·56 per cent. cadmium sulphate, 10° - 0·328; 40° - 0·283; 80° - 0·281. (2) 34·8 per cent. solution, 10° - 0·197; 40° - 0·190; 70° - 0·203. With cadmium iodide, negative values were obtained which were independent of temperature. L. M. J.

Electrical Resistivity of Electrolytic Bismuth at Low Temperatures and in Magnetic Fields. By JAMES DEWAR and JOHN AMBROSE FLEMING (*Proc. Roy. Soc.*, 1897, **60**, 425—432).—The authors have extended their observations (this vol., ii, 240) on the behaviour of electrolytically prepared bismuth, when cooled to very low temperatures and at the same time subjected to transverse magnetisation. The electrical resistivity of bismuth in C.G.S. units, transversely magnetised in a constant magnetic field, but at variable temperatures, is given in the following table:—

Temperature of the bismuth wire.	Out of the magnetic field.	In the magnetic field.		
		Strength 2,450 C.G.S. units.	Strength 5,500 C.G.S. units.	Strength 14,200 C.G.S. units.
+ 19°	116,200	123,500	132,000	187,000
− 79	78,300	105,000	158,000	284,000
− 185	41,000	186,000	419,000	1,740,000
− 203	34,300	283,500	—	—

It will be seen that if the transverse field is zero, cooling the bismuth always reduces its resistance. If, then, the bismuth is transversely magnetised, the resistance is increased, and for every temperature below the normal one, there is some particular strength of transverse field, which just annuls the effect of cooling, and brings the resistance of the bismuth back again to the same value it had when not cooled and when not in any magnetic field. The lower the temperature, the less is the strength of field which will bring the bismuth back to its original resistance when not cooled and not in the field.

These results indicate that at absolute zero bismuth should be converted into a non-conductor by a sufficiently strong transverse magnetisation. In this respect, bismuth is a remarkable exception to other metals.

The effect of transverse magnetisation at low temperatures was tried on zinc, iron, and nickel, but no effect was found sensibly greater at low than at ordinary temperatures, although these metals have their resistance affected by magnetisation to a small degree. At a temperature of about 150°, bismuth would probably cease to have its resistivity affected by a transverse magnetic field. H. C.

Dieletric Constant of Ice and Alcohol at very Low Temperatures. By JAMES DEWAR and JOHN AMBROSE FLEMING (*Proc Roy. Soc.*, 1897, **61**, 2—18).—The dielectric constant of ice is found to increase progressively from a value of about 2·8 to 11·6 between the limits $-198°$ and $-131°$ of the platinum thermometer. At absolute zero, the dielectric constant would probably not be far from 2·0. With relatively very slow reversals of electromotive force, the dielectric constant of ice at $-185°$ is a number not far from 2·9, which is not very different from that found by observers using reversals of many millions per second by the use of electrical oscillations or waves, when working at temperatures of 0° or a little below. On the other hand, the values found for ice at or a little below 0°, when using very slow oscillations, seems to indicate a dielectric constant of 78. It remains to be seen how the high value is connected with the low one, and whether this variation may be properly regarded as a case of anomalous dispersion.

The dielectric constant of solid alcohol at $-185°$ was found to be 3·12. The dielectric resistance of ice and frozen alcohol at and from the temperature $-185°$ was taken. With rising temperature, a rapid increase takes place in the conductivity of ice at about $-90°$, and in the case of alcohol as soon as a rise in temperature of about 10° has occurred, the conductivity begins to go up with great rapidity.

H. C.

Development of Heat by the Action of Bromine on Unsaturated Compounds.—By WLADIMIR F. LUGININ and IVAN KLABUKOFF (*Compt. rend.*, 1897, **124**, 1303—1306).—The authors have determined directly in the calorimeter the quantity of heat developed by the action of bromine on various allyl and allied derivatives in presence of carbon tetrachloride or alcohol. The results are as follows: Diallyl, 56,114 Cal. ($2 \times 28{,}057$); allylic chloride, 26,821; allylic bromide, 26,695; allylic alcohol, 27,732; allylic ether, 27,017

allylic acetate, 28,133; cinnamic alcohol, 22,321; crotonaldehyde, 19,349; and mesitylic oxide, 20,238. It is noteworthy that in the case of allylic alcohol and its derivatives the values are almost the same, and in the case of the bromide and chloride are practically identical. The substitution of phenyl for hydrogen in allylic alcohol reduces the heat developed by the action of bromine, and the presence of the ketonic or aldehydic function has a similar effect.

C. H. B.

Cryoscopic Observations on Acid Amides. By KARL AUWERS (*Zeit. physikal. Chem.*, 1897, **23**, 449—468).—The cryoscopic relations in naphthalene and benzene solutions were investigated for a large number of derivatives of aniline and its homologues, such as the anilides, and their halogen, nitro-, and alkyloxy-derivatives. Aniline, toluidine, anisidine, and the nitranilines all behaved normally, but abnormal values were obtained for most of the other compounds. In the anilides of the fatty acids, the molecular weight of the acid radicle has but little influence on the abnormality, the greatest deviation from normal values occurring with acetanilide. The general rules found by Innes and Orton as applying to the substituted phenols hold also for the compounds examined, that is, an ortho-substituent diminishes the abnormality, which is, however, in general increased by a para-group, and to a less extent by a meta-group. The acetyl compounds are in general more abnormal than the formyl compounds. The nitro-group has a powerful normalising influence in the ortho-position, but does not exert any abnormalising effect in the para-position; the normalising influence of methoxyl and the aldehyde group in the ortho-position is very marked. L. M. J.

Maximum Depression of the Freezing Point of Mixtures. By EMANUELE PATERNÒ and G. AMPOLA (*Gazzetta*, 1897, **27**, i, 481—536).—The authors have determined the freezing points of long series of mixtures of a number of pairs of organic compounds and find that in all the cases examined the freezing points of the mixtures are lower than those of the constituents of the mixture. The maximum depressions of the freezing points are given in the accompanying table, in which columns 1 and 3 state the components of the mixture and columns 2 and 4 give their respective melting points; column 5 states the percentage of the component named in column 1 in the mixture of lowest freezing point, and column 6 gives the melting point of the latter. Mixtures of thymol and trimethylcarbinol or water, and of benzene and paraldehyde were also examined, and conform to the general rule. Usually, the curve obtained by plotting freezing point against composition shows only one minimum, but in the case of mixtures of trimethylcarbinol and phenol it shows five. The minimum freezing point never corresponds with a mixture containing any definite proportion, and the freezing points of the mixtures cannot be even approximately calculated by Ostwald's method, which depends on the application of Van't Hoff's formula $\Delta = 2T^2/100\lambda$. In some cases, two definite freezing points for the eutectic mixture are obtained and frequently the minimum freezing point is lower than that of the eutectic mixture; the authors, although considering their results as

1.	2.	3.	4.	5.	6.
C_6H_6	5·53°	$pC_6H_4Me_2$	13·35°	55·22°	− 22·39°
,,	5·55	C_6H_5OH	40·24	59·13	− 5·275
,,	5·48	pC_6H_4BrMe	26·71	50·25	− 16·78
$pC_6H_4Me_2$	13·35	,,	26·74	60·78	2·39
$C_6H_5 \cdot OH$	40·06	,,	,,	42·76	13·41
Thymol	49·20	,,	,,	35·51	11·35
$C_2H_4Br_2$	9·91	,,	,,	57·87	− 6·67
$CMe_3 \cdot OH$	23·52	,,	,,	61·15	8·76
$C_2H_4(CO)_2NEt$	28·81	,,	26·73	55·15	0·54
$(CH_2Ph)_3N$	91·3	,,	,,	30·97	14·19
Veratrole	22·22	,,	,,	47·36	− 3·33
$C_2H_4Br_2$	10·00	$pC_6H_4Me_2$	13·35	67·26	− 18·85
Paraldehyde	11·24	,,	,,	38·10	− 14·14
$C_6H_5 \cdot OH$	40·24	,,	,,	37·04	5·575
Veratrole	22·40	,,	,,	51·01	− 4·0
$CH_3 \cdot COOH$	15·05	,,	,,	48·53	0·17
$C_2H_4(CO)_2NEt$	28·81	,,	13·28	63·72	− 2·63
Paraldehyde	12·03	$C_2H_4Br_2$	10·00	43·15	− 17·20
$C_6H_5 \cdot OH$	40·24	,,	,,	21·50	− 1·32
,,	,,	CH_2Ph_2	24·45	39·16	10·01
,,	,,	,,	24·68	38·68	11·52
Thymol	49·24	$C_6H_5 \cdot OH$	39·53	48·17	7·47
$CMe_3 \cdot OH$	24·95	,,	40·87	82·90	9·65
,,	,,	,,	,,	69·87	19·95
Thymol	49·32	$CH_3 \cdot COOH$	15·05	56·27	− 8·76

merely preliminary, do not think that this curious observation is due to experimental error. W. J. P.

Abnormal Freezing Point Depressions. By FELICE GARELLI (*Gazzetta*, 1897, **27**, i, 247—254).—The author combats Bodländer's criticisms (this vol., ii, 133) respecting his conclusions. (This vol., ii, 14). W. J. P.

Cryohydrates. By GIUSEPPE BRUNI (*Gazzetta*, 1897, **27**, i, 537—561).—The author gives a short summary of our knowledge of cryohydrates, and has experimentally investigated a number of cases; he determines the melting point of a cryohydrate by allowing it to freeze round a thermometer bulb and noting the temperature at which the thermometer remains stationary. The cryohydrate is prepared by taking a solution slightly more concentrated than that corresponding in composition with the cryohydrate, cooling it to the cryohydric temperature and dropping in crystals of ice and of the salt; the deposited cryohydrate is separated, melted, and again frozen as before in order to obtain material which has the cryoscopic composition, and is suitable for analysis.

Mixtures of the double salt, $ZnSO_4,K_2SO_4 + 6H_2O$, with excess of zinc sulphate give a cryohydric temperature of $-6·6°$, and with excess of potassium sulphate of $-1·7°$; the cryohydric temperature of zinc sulphate is $-6·4°$ and the cryohydrate contains 43·5 per cent. of $ZnSO_4$; the cryohydric temperature of potassium sulphate is $-1·55°$, the cryohydrate containing 7·4 per cent. of potassium sulphate, whilst the cryohydric temperature of the double salt is $-1·0°$, and the cryo-

hydric composition is 9·8 per cent. of $ZnSO_4,K_2SO_4$. The cryohydric solutions of mixtures of the double salt with one of its constituent salts have lower freezing points than the cryoscopic solution of the double salt or of the component salt present in excess.

By examining the isomorphous salts, zinc sulphate and magnesium sulphate, the author shows that the cryohydric temperature of a solution in equilibrium with mixtures of two perfectly isomorphous salts varies as the composition of the mixture of salts, the limits being the cryohydric temperatures of the single salts. Thus the cryohydric temperatures of mixtures of magnesium and zinc sulphates containing 100, 69·5, 58·8, 37·5, 19·6, and 0 per cent. of $MgSO_4$ are −5·2°, −5·5°, −5·5°, −6·0°, −6·2°, and −6·4° respectively.

The case of mixtures of three salts which are not isomorphous and do not form double salts was also examined, the salts selected being potassium chloride, nitrate, and sulphate. The accompanying table

Salts present.			Cryohydric temperature.	Composition of cryohydrate.		
A.	B.	C.		A.	B.	C.
KCl	—	—	−10·8°	24·9	0	0
—	KNO_3	—	−2·85	0	*12·6*	0
—	—	K_2SO_4	−1·55	0	0	7·4
KCl	KNO_3	—	−11·5	*24·5*	*4·5*	0
KCl	—	K_2SO_4	−10·9	*24·2*	0	*1·4*
—	KNO_3	K_2SO_4	−3·3	0	9·1	5·2
KCl	KNO_3	K_2SO_4	−11·55	24·5	4·5	1·3

summarises the results, the concentrations being expressed in parts by weight of salt per 100 of water; the numbers quoted in italics are those obtained by other workers. It follows that the cryohydric temperature of a solution in equilibrium with three non-isomorphous salts which do not form double salts is lower than the cryohydric temperatures of solutions in equilibrium with either two of the three salts.

W. J. P.

Molecular Volumes of Crystallised Carbohydrates. By JOSEPH PIONCHON (*Compt. rend.*, 1897, **124**, 1523—1524).—See this vol., i, p. 547.

Extension of the Law of Avogadro to Homogeneous Liquids. By ISIDOR TRAUBE (*Ann. Phys. Chem.*, 1897, [ii], **61**, 396—400).—As the author has shown in previous communications, the molecular co-volumes of homogeneous liquids are the same under similar conditions. Where exceptions to this rule are met with, they may be either traced to association in the liquids examined or to the influence of changes in the sphere of vibration of the atoms as shown by the refractions of the liquids (compare Abstr., 1896, ii, 235; and this vol., ii, 85).

H. C.

Solubility of Super-cooled Liquids. By LUDWIG BRUNER. (*Zeit. physikal. Chem.*, 1897, **23**, 542—544).—The solubility of an

over-cooled liquid cannot be identical with that of the solid, or two systems not in equilibrium with one another could be in equilibrium with a third system, and the author describes experiments proving the greater solubility of the liquid in cases where no water of crystallisation is present to affect the result. A hot saturated solution of hydrocinnamic acid is made and cooled, the acid separating in drops which remain liquid at ordinary temperatures; after the solution has been filtered from the drops of liquid acid, the introduction of a crystal of the solid acid or violent agitation causes the filtrate to crystallise; the solution saturated with respect to the liquid acid is supersaturated, therefore, with respect to the solid. Measurement with alkali showed the solubility of the liquid to be greater in the ratio 15 : 17. In super-cooled solutions of thymol also, the solidification of the liquid thymol below the water is immediately followed by the separation of crystals throughout the solution. Analogous results had been obtained by Alexéeff with salicylic and benzoic acids, which he had explained by the assumption of "isomeric solutions." L. M. J.

Velocity of Dissolution of a Solid in its own Solution. By ARTHUR AMOS NOYES and WILLIS RODNEY WHITNEY (*Zeit. physikal. Chem.*, 1897, **23**, 689—692).—In order to prevent any noticeable alteration of surface during the experiments, the solids were compressed into cylinders about 8 cm. long and 2 cm. in diameter. These were introduced into water, and the concentration determined from time to time. Experiments were performed with benzoic acid and lead chloride, and the dissolution-velocity was found to be given by the equation $dx/dt = C(S - x)$ where x is the concentration of the solution and S that of the saturated solution, C being a constant. The author considers the equation to really be that of diffusion, the film of liquid immediately in contact with the solid being a saturated solution which diffuses into the more dilute layers. L. M. J.

Solubility of Mixed Crystals and Magnitude of the Crystal Molecule. By ANDREAS FOCK (*Zeit. Kryst. Min.*, 1897, **28**, 337—413). —Van't Hoff has indicated that isomorphous mixtures or mixed crystals may be regarded as solid solutions; solid solutions must thus be treated as molecular mixtures. Roozeboom (Abstr., 1892, 265), by applying the theory of thermodynamical potential, showed that in the equilibrium condition at constant temperature and pressure, to each solid solution or isomorphous mixture of two substances corresponds a perfectly definite concentration of the two constituents in the liquid solution. It was then shown by Nernst (Abstr., 1890, 3) that his principle respecting the partitioning of a dissolved substance between two non-miscible solvents in equilibrium is applicable to the case of a solid solution in equilibrium with a liquid solution.

Let c_1 and c_2 be the number of gram-molecules per unit volume of two isomorphous salts, A and B, in a common liquid solution and x_1 and x_2 be the corresponding molecular concentrations in the solid solution of A and B with which equilibrium is established; then the partition coefficients c_1/x_1 and c_2/x_2 are in general constant and independent of the absolute concentration. If, however, the molecular weights are n times as great in the liquid as in the solid solutions, then it follows

from the law of mass-action that the ratios $c_1/x_1^{\frac{1}{n}}$ and $c_2/x_2^{\frac{1}{n}}$ or c_1^n/x_1 and c_2^n/x_2, where n is greater or less than unity, will be constant. These simple laws can only be expected to hold in dilute solutions, the gaseous laws not being applicable to concentrated solutions; further, in dilute solutions, the electrolytic dissociation must disturb the constancy of the partition coefficients. Thus, if binary electrolytes are dealt with, and γ is the dissociation coefficient of the saturated solution, then $c_1(1-\gamma)/x_1$, which refers only to the undissociated part, δ, of the electrolyte, is constant; as, however, the author has previously pointed out (Abstr., 1896, ii, 160), Nernst's principle, according to which the dissociation coefficients of two electrolytes in a common solution are equal, and equal to the dissociation coefficient referred to the total concentration, is sometimes applicable. If the total molecular concentration remains constant, so does the dissociation, and consequently c_1/x_1 remains as constant as $c_1(1-\gamma)/x_1$; but if the total concentration changes, the relation $c(1-\gamma)=\kappa c^2\gamma^2$ holds, where κ is the general equilibrium constant and c is the volume concentration. It results from this that the dissociation coefficient in general decreases with increasing concentration, and *vice versâ*. The above relations must hold if only the undissociated material in solution determines the saturation equilibrium, but whether this is a permissible assumption has not previously been decided; Noyes (Abstr., 1893, ii, 565) considers it probable that both the dissociated and undissociated substance in solution determine its saturation. If this is the case, then neither $c_1(1-\gamma)/x_1$ nor $c_1\gamma/\sqrt{x}$ is constant, but their sum, namely,

$$c_1[1+\gamma(\sqrt{x}-1)]/x_1.$$

The influence of temperature changes on the relations indicated above is also considered. It is pointed out that, since double salts are dissociated into their component salts in solution, and Avogadro's principle does not apply to the crystalline state, there is, up to the present, no evidence that double salts are molecular complexes having the molecular composition usually stated.

The author has examined a number of cases of equilibrium between solid and liquid solutions of pairs of isomorphous salts. The equilibrium was established by three methods (1) By spontaneous evaporation of the aqueous solution of the two salts until mixed crystals separate at a temperature constant within 2° or 3°; (2) by evaporating the mixed solution, keeping the temperature at 30° by an Ostwald thermostat, and (3) by adding the salt *B* to a solution of *A* saturated at 25°, dissolving by heat, cooling again to 25°, and separating the deposited mixed crystals. The solid solutions, after powdering, were shaken at 25° with the corresponding liquid solution for some hours in order to ensure complete equilibrium.

The following pairs of salts were examined thus :—(4) potassium and ammonium chlorides, (4) potassium and ammonium bromides, (2) potassium bromide and chloride, (4) potassium and thallium nitrates, (1) barium and lead nitrates, (1) potassium and ammonium sulphates, (1) potassium sulphate and chromate, (1) lead and barium formates, (4) copper and nickel sulphates, (1) lead and strontium hyposulphates, (1) potassium copper sulphate and ammonium copper sulphate, (2) copper ammonium sulphate

and nickel ammonium sulphate, (1) or (2) copper ammonium sulphate and zinc ammonium sulphate, and (1) potassium and thallium alums. The number prefixed to each case refers to its place in Roozeboom's scheme of classification (Abstr., 1892, 265) of equilibria between solid and liquid solutions. The salt-pairs, potassium bromide and iodide, and potassium chloride and iodide, were examined, but the results were inconclusive; the behaviour of carbamide and thiocarbamide showed these substances to be not isomorphous. The mixed solution of the rhombohedral double salts, $CdCl_2,4KCl$ and $CdCl_2,4NH_4Cl$, on evaporation, deposit crystals of a typically different double salt. Experiments on mandelic acid and its salts also led to no satisfactory results.

The quantitative results show clearly that the expression

$$c[1+\gamma(\sqrt{x}-1)]/x$$

is much more nearly constant in most cases than either $c(1-\gamma)/x$ or $c\gamma / \sqrt{x}$, thus demonstrating that the saturation of a liquid solution of an electrolyte is conditioned neither by the dissociated nor by the undissociated portion of the electrolyte alone; both the dissociated and undissociated part together determine the saturation of the solution.

The authors results further show that Nernst's solubility law, which states that the solubility of a salt decreases, if to its solution is added another salt having an ion in common with it, is erroneous; the exceptions to Nernst's law previously recorded have been attributed to the formation of molecular aggregates, but this the author shows to be untenable. It follows from this that Noyes' method of determining dissociation constants is not valid, although in many cases it may give approximately correct results. In place of Nernst's law, that the molecular concentration of the undissociated substance is a constant in mixed solutions, must be accepted the law that the sum of the concentration of the undissociated molecules and of the square of the concentration of the ions is a constant; this of course premises that no, or appreciably no, dissociation occurs in the solid solution. The new law is expressed by saying that $c[1+\gamma(\sqrt{x}-1)]$ is a constant for binary electrolytes; the relation is naturally more complex for ternary electrolytes. The principle holds that the solubility, or the equilibrium between several phases of variable composition, is governed by the law of chemical mass-action.

The conclusion clearly indicated by the author's work, namely, that the molecular weight in the crystalline state is identical with that of the chemical molecule, is of great crystallographic importance; it shows that Bravais' theory, that the molecules in a crystalline structure are disposed in parallel positions, is untrue, and consequently supports the later theory of Sohncke and Fedorow, which states that, in a crystalline structure, the arrangements of molecules is identical around each molecule.

Further, it is concluded that double salts and some salts containing water of crystallisation have not the molecular composition usually attributed to them; the constant proportion in which the various components of the solid salt separate together in the solid state is merely a result of the regular fitting together of those components in the crystal structure. W. J. P.

Permeation of Hot Platinum by Gases. By WYATT W. RANDALL (*Amer. Chem. J.*, 1897, **19**, 682—691. Compare Ramsay and Travers, *Chem. News*, 1897, **75**, 253).—A platinum tube closed at one end, about 35 cm. long and 3 mm. internal diameter, was connected by the open end to a mercury pump and vacuum-tube (the latter for spectroscopic observations), whilst the other end, to the extent of $\frac{2}{3}$ to $\frac{3}{4}$ of the length of the tube, was inserted into a piece of hard glass tubing which was heated to a white heat; a dry gas was passed through the space between the two tubes, and the nature of any gas that diffused through the hot platinum into the vacuum of the pump was examined spectroscopically. Hydrogen was found to permeate the hot platinum, but much less slowly than Graham's statements lead one to expect; neither of the constituents of air will permeate it, nor will methane, in spite of its low density. Hydrogen, purified by filtration in this way, still exhibits the "compound" spectrum. C. F. B.

Diffusion Constants of some Metals in Mercury. By GEORG MEYER (*Ann. Phys. Chem.*, 1897, [ii], **61**, 225—234. Compare Humphreys, Trans., 1896, 243).—Des Coudres has measured the rate of diffusion of zinc in mercury by charging the surface of the mercury electrolytically with zinc, and measuring the potential difference between the surface and a zinc electrode, as the zinc gradually diffuses through the mass of the mercury. By a modification of this process, the author has determined the rates of diffusion of zinc, lead, and copper in mercury. The results are given in the following table :—

	$k\ \frac{\text{cm.}^2}{\text{day}}$.	t.	K kg.	l mm.	$u\ \frac{\text{mm.}}{\text{sec.}}$
Zn	2·09	15·0°	$1·00 \times 10^9$	$0·231 \times 10^{-8}$	332·2
Cd	1·56	15·0	$1·35 \times 10^9$	$0·266 \times 10^{-8}$	253·1
Pb	1·37	15·6	$1·61 \times 10^9$	$0·270 \times 10^{-8}$	186·4
Au	0·72	11·0	$2·88 \times 10^9$	$0·137 \times 10^{-8}$	189·3

k is here the diffusion constant, and t the temperature, K is the force required to move the gram-atom with the velocity 1 cm./sec. through the mercury, l is the mean length of path, and u the mean velocity of the atoms. The data for gold are those of Roberts-Austen, and are inserted for the purpose of comparison. H. C.

Unit of Atomic Weights. By FRIEDRICH WILHELM KÜSTER (*Zeit. anorg. Chem.*, 1897, **14**, 251—255).—A protest against Seubert's proposal to retain hydrogen as the unit of atomic weights, making $O = 15·88$ (this vol., ii, 137), in place of accepting $O = 16$ as the standard value. H. C.

Basis of Atomic Weights. By BOHUSLAV BRAUNER (*Zeit. anorg. Chem.*, 1897, **14**, 256—262).—The author recapitulates the many advantages of accepting $O = 16$ as the basis of atomic weights, and opposes Seubert's proposal to adopt the system $H = 1$ and $O = 15·88$ (compare preceding abstract). H. C.

Determination of the Atomic Masses of Silver, Mercury, and Cadmium by the Electrolytic Method. By WILLETT LEPLEY HARDIN (*J. Amer. Chem. Soc.*, 1896, **18**, 990—1026).—Silver was deposited electrolytically from the nitrate, the acetate and the benzoate; the succinate was found to be unsuitable for the purpose. Ten observations were made in each case, and from the three series the final result Ag = 107·9275 was obtained (O = 16).

Mercury was deposited electrolytically from mercuric chloride, bromide, and cyanide, and, in addition, the ratio of the atomic mass of mercury to that of silver was determined by passing the same current through solutions of the two metals, and weighing the two deposits produced. The final result was Hg = 199·985 (O = 16).

Cadmium was deposited from the chloride and the bromide, the final result being Cd = 112·046 (O = 16).

H. C.

Equilibrium in Systems of Three Bodies, with Two Liquid Phases. By FRANS A. H. SCHREINEMAKERS (*Zeit. physikal. Chem.*, 1897, **23**, 649—666).—The general case of the equilibrium between three liquids is first considered and a general form of the binodal curve is given. As an example of three-liquid equilibrium, the case of water, chloroform, and ethylic alcohol at 20° is considered, and the diagram given shows the quantity of chloroform necessary to cause the separation of aqueous alcohol into two layers, and the ratio of alcohol/water above which the liquid always remains homogeneous. Draper's and Schuncke's experiments (Abstr., 1894, ii, 378) on the solubility of ethylic ether in aqueous hydrochloric acid supply some data for the construction of the binodal curve for the equilibrium of the system ethylic ether, water, hydrogen chloride. When one of the compounds is a solid, the form of the curve is different, and consists of a number of portions from which are derived the limits of composition necessary for separation into (1) solid and two liquid layers; (2) two liquid layers; (3) solid and one liquid; (4) homogeneous liquid. This case is exemplified by the equilibrium of ammonium sulphate, water, and ethylic alcohol, the theoretical deductions being in accord with the experimental results of Bodländer. Other solids besides ammonium sulphate cause aqueous alcohol to separate into two layers, such as sodium and potassium hydoxides, sodium phosphate, potassium and sodium carbonates, &c. Lescoeur considered one of the layers formed on adding potassium carbonate to aqueous alcohol to be a definite hydrate of the composition $(C_2H_6O)_2,H_2O$, due, the author points out, to the temperature not being varied during the experiments. De Forcrand found (Abstr., 1883, 961) that in the system chloroform, water, hydrogen sulphide, a solid phase occurs corresponding with the composition $CHCl_3,2H_2S,23H_2O$; moreover, at low temperatures, the vapour phase possessed a constant composition independent of the quantity of the liquid phases, a result which must hold at constant temperature for a phase of a system in equilibrium.

L. M. J.

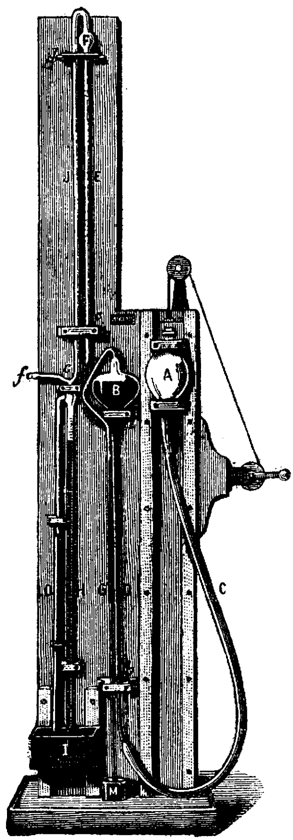
Equilibrium in the System; Water, Sodium Chloride, and Ethylene Cyanide. By FRANS A. H. SCHREINEMAKERS (*Zeit. physikal. Chem.*, 1897, **23**, 416—441).—The equilibrium in the system water,

and sodium chloride being known, that of water and ethylenic cyanide was first investigated, and the results are given in tabular form and as a curve. From these, it is seen that above 18·5° equilibrium exists between two liquid phases, that is, solution of the cyanide in water and of water in the cyanide, the critical point being 55°. At 42°, the densities of these two solutions are equal, so that the case exists of two liquids of equal density containing the same components but being non-miscible. At a higher percentage of cyanide, equilibrium between the pure compound and a solution of water in the cyanide is reached, so that at temperatures between 18·5° and 55° the addition of the cyanide gives the following states :—Solution of the cyanide in water, separation into two solutions, homogeneous liquid, separation into ethylenic cyanide and a solution of water in the cyanide. By the addition of salt, the region of equilibrium between the two solutions is extended, the critical point being 145°, the solution containing most cyanide being that with least salt. At the temperature 29°, a quintuple point exists where the phases, ethylenic cyanide, sodium chloride, solution 1, and solution 2 are in equilibrium. The various cases of equilibrium are fully discussed in the paper and illustrated by numerous diagrams. L. M. J.

Application of the Phase-Law to Researches on Organic Additive Products. By Basil B. Kuriloff (*Zeit. physikal. Chem.*, 1897, **23**, 673—685).—The author first investigated the solubility relations of β-naphthol and picric acid in a manner identical with that employed for the researches on triphenylmethane and benzene (this vol., i, 573). The curve again exhibits the three branches, namely, where the solid phase is (1) picric acid (2) the compound $C_6H_5(NO_2)_3 \cdot OH, C_{10}H_7 \cdot OH$, (3) β-naphthol, and with two quadruple points where the curves 1, 2, and 2, 3 cut one another. A maximum of temperature, 157°, occurs at the point where the composition represented is that of the compound, the curve on each side of this point giving the lowering of the melting point of the compound by addition of (1) β-naphthol, (2) picric acid, so that the cryoscopic relations are entirely in accord with the existence of the compound of melting point 157°. In the case of picric acid and benzene, however, although the curve still consists of the three portions corresponding with the three solid phases, there is no maximum, but at the point where the composition represented is that of the compound, the curve changes in direction and becomes that representing the lowering of the freezing point of the picric acid, that is, the melting point of the compound is also the quadruple point. Observations of the boiling point of solutions of β-naphthol in benzene gave a normal molecular weight, so that the tendency to form a compound is not apparent in boiling point observations. In the case of mixtures of benzene and β-naphthol, no compound is formed, the curve consisting solely of the two parts, namely, where the solid phase is (1) β-naphthol, (2) benzene. L. M. J.

Explanation of the Deviations from the Normal Course of Reaction in the Case of Solutions. By Ernst Cohen (*Zeit. physikal. Chem.*, 1897, **23**, 442—448).—The inversion of cane-sugar by acids does not follow the normal course of a monomolecular reaction, but

the velocity constant is greater at high than at low concentrations. Thus, at 25°, with N/2 hydrochloric acid, the values are, 40 per cent. – 29·16, 20 per cent. – 22·87, 10 per cent. – 20·63, 4 per cent. – 19·15. The author considers that these deviations are due to the same cause as deviations from Boyle's law, that is, to the volume of the sugar molecules, which, if not allowed for, would have the effect of increasing the constant at high concentrations. If the acid remain the same, and b_{40} and b_{20} be the percentage volumes of the sugar in the 40 and 20 per cent. solutions, then $k_{40}/k_{20} = (100 - b_{20})/(100 - b_{40})$ from which, assuming $b_{40} = 2b_{20}$, and using the above values of k, the result $b_{20} = 17·7$ is obtained. From this, the values b_{10} and b_4 are calculated, and give the ratio $k_{10}/k_4 = 1·058$, that found experimentally being 1·077. Further researches to test the validity of the explanation were made with 30 per cent. and 15 per cent. solutions, which gave the value $b_{15} = 13·27$ leading to the same value as before for b_{20}. From the expression $k_p/k_q = c_p(100 - b_q)/c_q(100 - b_p)$ where c_p and c_q are the acid concentrations, the author deduces that a 12·5 per cent. solution should be inverted by N/16 hydrochloric acid at the same rate as a 25 per cent. solution by (N/16 ÷ 1·14) acid. The experimental results were in complete accord with theory, the rotation of the second solution remaining throughout double that of the first. From the values of b_{20} and b_{10}, the ratio k_{20}/k_{10} should be 1·10, and this was tested by the inversion with acids of various strengths, the ratio of the constants obtained being respectively 1·12, 1·11, 1·10, 1·10, 1·10; this is in complete accord with the theory. L. M. J.



Mercury Pump without Stopcocks or Movable Joints. By H. Henriet (*Compt. rend.*, 1897, **125**, 22—23) and Chabaud, *ibid.*, 107).—In this pump, valves and stopcocks are replaced by columns of mercury, and arrangements are made so that the first part of the exhaustion can be effected with a water pump. It will be readily understood from the illustration. The reservoir B terminates below in a vertical tube D which is connected with movable reservoir A. From the upper part of the tube D, just below its junction with B, there issues horizontally the tube E which is bent at right angles so that it is vertical, and returns on itself J, and terminates in a manometer tube H, at the junction with which

the tube *f*, for connecting with the vessel to be exhausted, issues horizontally. The upper part of the tube O, parallel with the manometer, is of glass, but the lower part is of caoutchouc for making connection with the water pump; when the water pump is disconnected, the caoutchouc tube is placed under the mercury in the same trough as the manometer. When A is lowered, the mercury runs out of B, and air enters at *f* and travels along J and E into B; when A is raised, the mercury rises in E and cuts it off, whilst the air in B is expelled through G and escapes through the small trough M.

CHABAUD states that pumps constructed on similar principles have been in use in several laboratories for some time. C. H. B.

A New Bottle for Washing Gases. By JOHANN WALTER (*J. pr. Chem.*, 55, 507—508).—In this apparatus, the gas to be washed first passes down a vertical tube in the usual way; the bubbles issuing from it then separately enter the lower end of a worm surrounding the vertical tube of the bottle. In this way, the gas rises slowly through the worm in separate bubbles, and is thoroughly washed.

J. F. T.

Inorganic Chemistry.

Action of Light on Mixtures of Chlorine and Hydrogen. By E. J. Armand Gautier and H. Hélier (*Compt. rend.*, 1897, **124**, 1267—1273; by Marcellin P. E. Berthelot, *ibid.*, 1273—1276, and by Armand Gautier, *ibid.*, 1276—1278).—When carefully dried hydrogen and chlorine in approximately equal volumes are exposed to diffused daylight (November) for a day, the proportion of hydrogen chloride formed is only about 2·55 per cent. of the mixture, whilst with the moist gases under similar conditions the quantity of hydrogen chloride may be as much as 60 per cent. When exposed for an hour to somewhat diffused autumn sunlight, the percentage of combination was 6·7 in the dry gases and 92·5 in the moist gases. It is clear, therefore, that the presence of water greatly accelerates the combination, a result probably due to the formation of intermediate products such as hypochlorous acid.

When the dry gaseous mixture was exposed at a distance of a metre to albo-carbon lights equivalent to 14·5 carcels, the percentage of combination was 92·5 after 237 hours. The rate of formation of hydrogen chloride at first increased until it reached a maximum of 2·8 per cent. per hour after 3 hours' exposure, and then it somewhat rapidly decreased, but neither in these cases nor in other exposures made to autumn sunlight was there any indication of a limit to the combination, and in this respect the action of light differs markedly from that of heat. With sunlight, the maximum rate of formation of hydrogen chloride is reached much more rapidly than with artificial light.

After the maximum has been passed, the rate of formation is not proportional to the number of uncombined hydrogen and chlorine atoms left in the mixture, because the hydrogen chloride already formed exercises a distinct retarding influence, although it does not limit the action.

In presence of an excess of chlorine, combination takes place more rapidly. With a mixture of Cl, 54·8 vols., H, 42·8 vols., and air 2·6 vols., combination was complete after 31 hours' exposure to the albo-carbon light, whilst with equal volumes of hydrogen and chlorine under similar conditions more than 250 hours were required. Excess of hydrogen has a similar, but less strongly marked, effect (compare this vol., ii, 437).

BERTHELOT considers that, in all investigations on the combination of mixed gases, it is essential to take into account possible reactions between the gases or the products of their combination and the material of the walls of the containing vessel (for example, the action of water on glass). In some cases, the combination of the gases and the action on the walls of the vessel may be simultaneous and not successive, the occurrence of any change at all being determined by the simultaneous action of chemical stresses between the gases and the material of the walls, which together constitute a heterogeneous system. Such local action on the walls will give rise to local thermal disturbances, and these may alter the nature or rate of the change in those regions. They may also lower the initial temperature at which changes will take place. Further, the reaction may be affected by the condensation of a film of gas on the surface of the containing walls. It is, in fact, the action of surfaces rather than the action of masses that has to be considered, and it is the surface actions that determine the equilibrium of the system.

GAUTIER replies that Berthelot's observations refer to his earlier experiments on the combination of gases when heated rather than to the present paper on the action of light on gases. He considers that the function of the walls of the vessel, which, in his experiments, were kept at a constant temperature and were not allowed to become heated by the combination, is to regulate the velocity of combination, and not to limit it. The phenomena with carbonic oxide and oxygen are similar to those with hydrogen and oxygen, but in the former case it is impossible to assume the formation of hydrates. Moreover, the results are the same with vessels of glass, silvered glass, porcelain, or quartz, and are not affected by different methods of cleaning and washing the internal surfaces. C. H. B.

Rendering Oxygen Active during the Slow Oxidation of Sodium Sulphite. By W. P. JORISSEN (*Zeit. physikal. Chem.*, 1897, **23**, 667—672).—The increased activity of oxygen during the oxidation of sulphurous acid or metallic sulphites had been previously observed by Mohr, Liebig, and Wicke. The author, therefore, endeavoured to ascertain whether in this case, as in those previously determined (this vol., ii., 253), the quantity of oxygen rendered active is equal to that used for the oxidation. Preliminary experiments showed that, during the oxidation of sodium sulphite by exposure to air, the quantity of

oxygen used is precisely that necessary for the conversion of the sulphite into sulphate. A solution of sodium sulphite, potassium hydrogen carbonate, and arsenic trioxide was next exposed to air, and it was found, in accordance with Mohr's experiments, that, in this case, the arsenic trioxide also oxidises, and that if a sufficient quantity of the carbonate is employed, the total quantity of oxygen used is double that required by the sulphite alone, and is independent of the quantity of the trioxide, so that here also the oxygen rendered active is equal in amount to that required by the sulphite itself. The author does not consider that the known facts justify the conclusions of Ihle and Bach regarding the cause of this increased activity. (Compare this vol., ii, 401, 402). L. M. J.

Tables of the Specific Weight of Solutions of Sulphur in Carbon Bisulphide. By GEORGE J. PFEIFFER (*Zeit. anorg. Chem.*, 1897, **15**, 194—203).—A Sprengel-Ostwald's pyknometer was employed in the determinations, and in order to prevent the evaporation of the bisulphide, the capillary tube of the pyknometer was closed with a drop of water when full to the mark with the solution at 15°. It was then placed in ice-cold alcohol, and the drop of water absorbed by filter paper. After the solution had contracted, the apparatus was washed with cold ether, dried, and weighed. The results are tabulated.
E. C. R.

Action of Telluric Chloride and Fluoride on the Corresponding Hydracids. By RENÉ METZNER (*Compt. rend.*, 1897, **125**, 23—26).—When hydrogen chloride is passed into a solution of tellurium chloride in a concentrated solution of hydrochloric acid at $-23°$, no precipitate forms, but if the liquid is cooled to $-30°$, the compound $TeCl_4,HCl + 5H_2O$ separates in slender, lemon-yellow needles, resembling the hydrobromide of the bromide (following abstract). It readily decomposes, with loss of hydrogen chloride.

When tellurous anhydride is dissolved in concentrated hydrofluoric acid, the liquid concentrated, the crystalline residue dissolved in hydrofluoric acid, and the liquid saturated with hydrogen fluoride at $-20°$, the compound $2TeF_4,3TeO_2 + 6H_2O$ separates in long, transparent crystals. When heated in hydrogen, they decompose, all the tellurium being converted into tellurous anhydride, and all the fluorine into hydrogen fluoride.

When the mother liquor from the preceding compound is more strongly cooled, with frequent stirring, the walls of the vessel being rubbed, the compound $TeF_4,TeO_2 + 2H_2O$ separates in large needles; like the preceding compound, it is decomposed by water. When heated, it yields tellurous anhydride and hydrogen fluoride.

The method adopted for analysing both these oxyfluorides is described in detail.

Telluric fluoride crystallises from its solution when the latter is saturated with hydrogen fluoride at $-50°$ and is cooled for a short time to $-70°$; the crystals, when once formed, melt very slowly, even at $-23°$. The formation of a hydrofluoride of the fluoride seems to require a very low temperature. C. H. B.

Combination of Telluric Bromide and Iodide with the Corresponding Hydracids. By RENÉ METZNER (*Compt. rend.*, 1897, **124**, 1448—1451).—If tellurous anhydride is dissolved in a cold saturated solution of hydriodic acid, and hydrogen iodide passed into the liquid, heat is developed, and black, quadratic needles with a metallic lustre separate, the yield being much greater if the liquid is cooled so that a large quantity of hydrogen iodide is dissolved. The crystals have the composition $TeI_4,HI + 8H_2O$; they do not fume in the air, but are deliquescent, changing rapidly to a deep brown, viscous liquid. When heated out of contact with air, they melt constantly at 55°, and at a higher temperature, lose water and hydrogen iodide, a grey metallic-looking residue of telluric iodide being left. This iodide, when heated in the air, decomposes with incandescence, iodine being liberated, and tellurous anhydride formed.

The bromine compound is obtained in a similar manner, the liquid preferably being cooled to −15°. It forms slender, red, prismatic needles of the composition $TeBr_4,HBr + 5H_2O$. They remain unchanged for a long time in an atmosphere of hydrogen bromide, melt at 20° with liberation of hydrogen bromide, and fume and deliquesce in moist air. C. H. B.

Phosphorus Iodides. By J. ADOLPHE BESSON (*Compt. rend.*, 1897, **124**, 1346—1349).—Phosphorus tri-iodide is best prepared by the action of dry hydrogen iodide on phosphorus trichloride either alone or in presence of carbon tetrachloride. It melts at 61°, and is completely decomposed by water without liberation of iodine or formation of any insoluble product. Under a pressure of 15 mm., it begins to sublime below 100°, and sublimation becomes active at 120°, but if this temperature is exceeded, there is danger of decomposition. When dissolved in carbon bisulphide, the tri-iodide is reduced by mercury, the first product being the iodide P_2I_4, but with excess of mercury the ultimate products are mercurous iodide and a double mercury phosphorus iodide; this reaction is useful for the removal of the tri-iodide from mixed solutions. Silver behaves similarly, but the reduction stops at the di-iodide.

Phosphorus di-iodide melts and slightly decomposes at 110°. Under a pressure of 15 mm., even below 100°, it gives a sublimate of the tri-iodide, and the decomposition is more rapid at 120°, a residue of amorphous phosphorus being left. When treated with mercurous chloride, the di-iodide yields phosphorus trichloride, mercurous iodide, and phosphorus, the latter being entirely insoluble in carbon bisulphide. It is probable that in Gautier's reaction of the di-iodide with silver chloride, the phosphorus is likewise liberated in the amorphous form.

When a solution of iodine in carbon tetrachloride is added to carbon tetrachloride at the bottom of which there is a layer of fused phosphorus, the iodine is converted into phosphorus di-iodide, which remains in solution, and the phosphorus becomes covered with a layer of amorphous phosphorus. Some phosphorus is, of course, also dissolved by the tetrachloride, and the solution seems to contain an unstable compound, P_3I_4, which is decomposed by light, heat, or the concentration of the solution yielding amorphous phosphorus and the di-iodide,

which is again converted into the unstable compound, this cycle of changes constituting the mechanism by which white phosphorus is converted into the amorphous form. C. H. B.

Calcium Fluoride in a Fossil Elephant's Bone from the Tertiary. By JACOBUS M. VAN BEMMELEN, A. SIMON-THOMAS, and EDUARD A. KLOBBIE (*Zeit. anorg. Chem.*, 1897, **15**, 84—89).—The research was undertaken in order to determine if the bones from the strata in which Dr. E. Dubois discovered the remains of *Pithekanthropos erectus* contain fluorine and phosphoric acid in the ratio which has been determined by Carnot for Pliocene remains. The ratio for the air-dried substance was found to be 0·0478, for apatite it is 0·0892 : $\frac{0·0478}{0·0892} = 0·53$. Carnot, for bones from the Pliocene, gives the ratio 0·58. The authors point out that too much dependence must not be placed on these ratios, as the absorption of fluorine is not only dependent on the time (age of the strata), but also on the nature of the strata and the composition of the water flowing through the strata. E. C. R.

Absorption of Calcium Fluoride, Lime, and Phosphates in Fossil Bones. By JACOBUS M. VAN BEMMELEN and EDUARD A. KLOBBIE (*Zeit. anorg. Chem.*, 1897, **15**, 90—122).—The microscopical examination of a tibia of a fossil Stegodon shows that the outside is composed of a hard crust of calcium carbonate. In the compact portion, the Hafer's canals are filled with white, crystalline calcium carbonate, whilst in the outside portion many of the canals are filled with pyrites ; the inner portion of the compact part is bright brownish-yellow and free, or almost free, from pyrites. In the spongy portion, pyrites is also present, and the holes are entirely filled with calcium carbonate sometimes containing pyrites. In the axial hole of the spongy portion, the structure is almost entirely destroyed, and the sides of the hole covered with large crystals of calcium carbonate. The compact portion gave, on analysis, 30·3 P_2O_5, 1·45 F, 6·11 CO_2, 0·1 K_2O, 49·14 CaO, 0·31 MgO, 1·28 MnO, 0·61 Fe_2O_3, 0·41 FeS_2, 0·05 insoluble, 2·2 organic substance, 4·21 H_2O at 110° and 4 per cent. H_2O at a higher temperature. A sample containing some of the spongy portion gave 27·77 P_2O_5, 1·33 F, 8·61 CO_2, 0·06 K_2O, 48·08 CaO, 0·3 MgO, 1·25 MnO, 0·65 Fe_2O_3, 2·55 FeS_2, 0·35 insoluble, 1·7 organic substance, 3·7 H_2O at 110° and 4 per cent. of water at a higher temperature. The compact portion has the sp. gr. = 2·2. The structure of the bone is not altered. A consideration of the above analyses taken in conjunction with the high specific gravity and the fact that the structure of the bone is unaltered, points to the conclusion that there has been an absorption from the water of the strata, not only of calcium carbonate, but also of calcium phosphate into the compact portion. A portion of the calcium carbonate is converted into calcium fluoride (3 per cent.), also about half the magnesium phosphate and a small portion of the calcium phosphate is converted into manganese and ferric phosphates. The phosphate, by the absorption of lime, has become basic to such an extent that one-eighth more base is present than is required for the ratio 2 mols. orthophosphate to 1 mol. base. The absorption of these compounds is due to

the original phosphate in the bone; they do not form a chemical compound, but a hydrated absorption complex. E. C. R.

Action of Zinc on Hydrogen Chloride Dissolved in Organic Solvents. By F. Zecchini (*Gazzetta*, 1897, **27**, i, 466—473).—The author has examined the action of zinc on solutions of hydrogen chloride of known concentration in methylic, ethylic, and amylic alcohols and in acetone and ethylic ether; the zinc was allowed to act for a known length of time and the amount of hydrogen chloride decomposed determined by titration with standard potash. The zinc used was in the form of cylinders exposing 278 sq. mm. of surface and the solution was kept agitated and at the constant temperature of 20° during the experiment; the organic solvents used were carefully dehydrated, and the solutions being of one-half or one-third normal concentration in hydrogen chloride. The anhydrous solutions of hydrogen chloride in methylic alcohol, ethylic alcohol, and acetone in all cases acted rapidly on the zinc, and in some cases more rapidly than did an aqueous solution of hydrogen chloride of the same concentration; the addition of small quantities of water to the organic solutions of hydrogen chloride causes them to act less rapidly on the zinc. Dry amylic alcohol solutions of hydrogen chloride act very slowly on the metal.

The dry ethylic ether solutions of hydrogen chloride act far more rapidly on zinc than do aqueous solutions of the same concentration, and the addition of about 0·5 per cent. of water causes the action to proceed some four times as rapidly as before. This behaviour of ethereal solutions of hydrogen chloride is very remarkable in connection with the electrolytic dissociation hypothesis according to which the reactivity of an acid is measured by its dissociation. Hydrogen chloride is not dissociated in ethereal solution, yet it acts much more rapidly on zinc in ethereal than in aqueous solutions of the same concentration. W. J. P.

Basic Cupric Salts and Brown Cupric Hydroxide. By Paul Sabatier (*Compt. rend.*, 1897, **125**, 101—104).—The author uses the term *principal basic salts* to denote those salts which are formed by the direct action of the oxide or hydroxide on solutions of the normal salt. The principal basic salts of copper are of the type $CuR_2,3CuO + 3H_2O$, except that the sulphate contains $4H_2O$. The acetate is an exception and is of the type $CuR_2,2CuO + 2H_2O$.

All these salts except the acetate contain the bivalent group Cu_4O_3, and it appears probable that the same group is present in the brown hydroxide formed by the spontaneous dehydration of the blue hydroxide. This brown product has the composition $Cu(OH)_2,3CuO$, or $Cu_4O_3(OH)_2$. As a matter of fact, this brown hydroxide readily forms the principal basic salts when placed in contact with solutions of normal cupric salts. The basic nitrate thus obtained is crystallised in minute rhombic or hexagonal lamellæ derived from a monoclinic prism; when left in contact with the nitrate solution, the lamellæ change into needles. The blue hydroxide yields the same basic salt, but in an amorphous form. The basic chloride formed under similar conditions is amorphous; the basic bromide forms small, deep green, hexagonal lamellæ; the basic sulphate forms small, elongated prisms; the basic

dithionate crystallises in small, hexagonal lamellæ, and the basic chlorate in microscopic rhombic plates.

Solutions of the acetate and of the perchlorate, on the other hand, have no action on the brown hydroxide. C. H. B.

Action of Ammonia on Mercurous Iodide. By MAURICE FRANÇOIS (*J. Pharm.*, 1897, [vi], **5**, 388—392).—Ammonia acts on mercurous iodide in the cold, yielding metallic mercury and ammoniacal mercuric iodide, $HgI_2,2NH_3$; the latter is colourless, and is only stable in the presence of an excess of ammonia. The reaction was followed quantitatively by extracting the products with ether, which dissolves out the ammoniacal mercuric iodide.

If a large excess of ammonia is used, dimercuryammonium iodide and tetramercuryammonium iodide are formed.

Mercurous chloride appears to react with ammonia in much the same manner, and it is probable that the grey product formed consists of a mixture of free mercury and of one of the already known compounds of mercuric chloride with ammonia. J. J. S.

Atomic Weight of Cerium. By GREGOIRE N. WYROUBOFF and AUGUSTE V. L. VERNEUIL (*Compt. rend.*, 1897, **124**, 1300—1303).—The only cerium compound available for accurate determinations of the atomic weight is cerium sulphate, $3CeSO_4 + 8H_2O$. The composition of the hydrated salt is very constant, and the atomic weight may be determined from the loss of water at about 250°, or the loss of sulphuric anhydride at a higher temperature, the ratio of the residual oxide, Ce_3O_4, being calculated to either the anhydrous or hydrated salt.

Cerium prepared in different ways from monazite and cerite, and purified in the manner previously described (this vol., ii, 452), has an atomic weight of 92·70 to 92·87 [Ten determinations; standard not stated], these figures being probably accurate to within 0·2 or 0·3 per cent. C. H. B.

A Process of Oxidation and Chlorination [by Manganese Salts]. By ANTOINE VILLIERS (*Compt. rend.*, 1897, **124**, 1349—1351). —When a mixture of equal volumes of a saturated solution of oxalic acid, hydrochloric acid of 25 per cent., and nitric acid of 25 per cent. is heated, there is no evolution of gas, but if a small quantity of any manganese salt is added there is an almost immediate reaction with evolution of carbonic anhydride and nitrogen, and the decomposition proceeds even if heating is discontinued. If the nitric acid is in excess, the oxalic acid is completely oxidised. With more concentrated solutions, the oxalic acid is slightly decomposed even in absence of manganese, but the difference produced by the addition of manganese is very marked. Many other compounds of the fatty group, such as glucose and saccharose, behave in the same way. Compounds of the benzene group, on the other hand, yield chlorine substitution products instead of oxidation products; benzene and toluene, for example, yield chlorobenzene and chlorotoluene respectively, even at the ordinary temperature.

This property of transferring oxygen from one compound to another, possessed in so marked a degree by even small quantities of manganese,

is of special interest in connection with the co-existence of manganese and oxidising ferments in vegetables, as observed by Bertrand (following abstract). The decomposition of oxalic acid, in the manner described, has many points of resemblance to oxidations produced by oxidising ferments, and may perhaps be regarded as an example of "inorganic fermentation." C. H. B.

Oxidising Action of Manganese Salts: Constitution of Oxydases. By GABRIEL BERTRAND (*Compt. rend.*, 1897, **124**, 1355—1358).—All manganese salts have the property of bringing about the oxidation by atmospheric oxygen of solutions of quinol, pyrogallol, and paramidophenol, guaiacum, and similar substances. The solution acquires a colour which depends on the nature of the carbon compound, whilst the intensity of the coloration depends on the nature of the acid in combination with the manganese. Oxidation is much more energetic with salts such as the succinate, gluconate, or salicylate than with the chloride, sulphate, or nitrate.

Manganese salts in aqueous solution are partially hydrolysed, the degree of hydrolysis being greater with feeble organic acids than with inorganic acids. The manganous oxide oxidises in contact with air, and this change involves the splitting up of the molecules of atmospheric oxygen, one atom of the molecule combining with the manganous oxide, whilst the other atom is free to combine with any other oxidisable substance with which it may come in contact. The latter may, under these conditions, be oxidised, although it would resist the action of oxygen in the form of molecules. Quinol, when mixed with manganous oxide and agitated with air, is oxidised to quinone, and manganese peroxide is formed. In presence of acids, the manganese peroxide is converted into a manganous salt, a further quantity of the carbon compound being oxidised at the same time. If manganese peroxide is suspended in a dilute acid which has no action on it at the ordinary temperature, and quinol is added, then the manganese dissolves and quinone is formed.

These results, and those previously described, tend to the view that the oxydases are special compounds of manganese in which the acid radicle, of a proteid character and varying with the particular ferment, has just sufficient activity to keep the metal in solution, whilst the metal is the real carrier of oxygen. C. H. B.

Function of Manganese in Certain Oxidations. By ACH. LIVACHE (*Compt. rend.*, 1897, **124**, 1520—1521).—The author points out that the influence of manganese in promoting the oxidation of organic substances as described by Villiers and by Bertrand (preceding abstracts), is similar to the effect that he observed some years ago (Abstr., 1884, 532) in the case of drying oils, and the explanation is doubtless the same in all cases. C. H. B.

Constitution of Inorganic Compounds. No. IX. Triammine and Diammine Cobaltic Salts. BY ALFRED WERNER (*Zeit. anorg. Chem.*, 1897, **15**, 143—172).—The triammine salts are prepared from dichloroaquotriammine cobaltic chloride, which is separated from the small quantity of tetrammine salt, formed during its preparation, by

treating it with mercuric chloride, whereby the tetrammine salt is precipitated as an insoluble mercury double salt.

Acid dichloraquotriamminecobalt sulphate, $[Co(NH_3)_3H_2OCl_2]SO_4H$, is obtained by mixing the dichloraquotriammine chloride to a thin paste with a cooled mixture of concentrated sulphuric acid (2 vols.) and concentrated hydrochloric acid (1 vol.), and after the mixture has remained 1 hour, spreading the paste on a porous plate. This operation is repeated three times, and the product then washed with alcohol until free from acid, and dried over sulphuric acid. It is a greyish-green, crystalline powder, and dissolves fairly easily in water yielding a green solution which quickly changes to indigo blue; the solution has an acid reaction. It is obtained in black, lustrous, prismatic crystals by adding concentrated sulphuric acid to the cold concentrated aqueous solution and evaporating the clear liquid in a vacuum over sulphuric acid. The *silver* derivative is obtained by thoroughly mixing the acid sulphate with a small quantity of silver nitrate solution and washing the product with absolute alcohol. It is a grass green powder which quickly decomposes and darkens, and when treated with water decomposes with separation of silver chloride.

Dichloraquotriamminecobalt nitrate, $[Co(NH_3)_3H_2OCl_2]NO_3$, is obtained by treating the dichloro-chloride with concentrated nitric acid, and washing the greyish-green precipitate with alcohol and ether until free from acid. It dissolves in water, forming a green solution which quickly changes to blue.

Bluish-grey chloraquotriamminecobalt sulphate,

$$[Co(NH_3)_3(H_2O)_2Cl]SO_4,$$

is obtained by dissolving the above acid sulphate in water and precipitating the indigo-coloured solution with an equal volume of alcohol. It dissolves in water with an indigo-blue coloration, and, if kept, the solution deposits crystals of the sparingly soluble violet salt described below. When the solution is treated with hydrochloric acid, dichloraquotriamminecobalt chloride is obtained.

Grey dichloraquotriamminecobalt chloride, $[Co(NH_3)_3H_2OCl_2]Cl$, is obtained by treating the preceding salt with concentrated hydrochloric acid. It has the same percentage composition as the dichro-cobalt chloride, but is not identical with that salt. It dissolves in water, forming a pure blue solution which changes to violet, whereas the dichro-cobalt chloride yields a green solution which changes to blue and then violet. When treated with concentrated nitric acid, it yields a nitrate which gives a green solution gradually changing to blue, and then to violet. The nitrate obtained from the dichro-cobalt chloride also yields a green solution, but this changes to blue and violet more quickly than the preceding nitrate.

Violet chlorodiaquotriamminecobalt sulphate, $[Co(NH_3)_3(H_2O)_2Cl]SO_4$, is obtained by heating an aqueous solution of the acid sulphate on the water bath and allowing the solution to crystallise in a vacuum. It separates in small, lustrous crystals, is almost insoluble in water, and can also be obtained by treating the following salt with sulphuric acid.

Chlorodiaquotriamminecobalt chloride, $[Co(NH_3)_3(H_2O)_2Cl]Cl_2$, is obtained by treating the preceding salt with concentrated hydrochloric

acid. It is a dark-violet, crystalline powder, and dissolves in water to a pure violet solution. When treated with nitric acid, the corresponding *nitrate* is obtained as a bright violet, crystalline powder. When warmed with hydrochloric acid, dichloraquotriamminecobalt chloride is obtained.

Sulphatodiaquotriamminecobalt sulphate, $[Co(NH_3)_3(H_2O)_2SO_4]_2SO_4 + H_2O$, is obtained by adding the requisite quantity of silver sulphate to a warm, concentrated solution of dichloraquotriamminecobalt chloride, and evaporating the filtrate from the silver chloride in a vacuum. The residue is extracted with water, when the salt is left undissolved; by evaporating the solution and again extracting with water, a further quantity of the insoluble salt is obtained. It is a reddish-violet powder, insoluble in water, but soluble in concentrated hydrochloric, nitric, and sulphuric acids. When mixed with concentrated hydrochloric acid, it yields chlorodiaquotriammine sulphate, and by the prolonged action of the acid, the dichloraquocobalt chloride.

Oxalodiaquotriamminecobalt nitrate, $[Co(NH_3)_3(C_2O_4)(H_2O)_2]NO_3$, is obtained by treating dichloraquotriamminecobalt chloride with a cold saturated solution of oxalic acid, and, after adding an equal volume of alcohol, warming the mixture for one minute. On cooling, oxalochlorotriamminecobalt crystallises out. This is treated with the theoretical quantity of silver nitrate and the filtrate allowed to crystallise. It crystallises in silky, carmine-red crystals, and is sparingly soluble in cold water, easily so in warm water. When warmed for a short time with hydrochloric acid, it is converted into *chloroxaloaquotriamminecobalt*, $Co(NH_3)_3ClHO_2(C_2O_4)$, which is a violet powder, insoluble in water. When treated with a few drops of acetic acid and sodium nitrite, it yields *nitroxalotriamminecobalt*, $Co(NH_3)_3C_2O_4 \cdot NO_2$, which is a cherry-red, crystalline powder insoluble in water.

Derivatives of the diamminecobaltic series are prepared from potassium tetranitritodiamminecobalt, which is prepared by Jörgensen's method (*J. pr. Chem.*, [ii], **23**, 249), somewhat modified, as follows: 500 c.c. of a neutral solution of cobalt carbonate (20 grams) in hydrochloric acid is treated with ammonium chloride (100 grams) and the mixture heated to 50°; a solution of pure potassium nitrite (250 grams) in water (250 c.c.), also heated to 50°, is then gradually added, and the mixture kept at 40—50°, for 20—30 minutes, and allowed to cool. After 24 hours, the prismatic crystals of the potassium salt are washed free from the fine, greenish-yellow precipitate, and recrystallised from water. It is most important that the potassium nitrite should be pure. If less potassium nitrite is employed, or the mixture heated for a longer time at 50—60°, a mixture of potassium tetranitritodiamminecobalt with trinitritotriamminecobalt is obtained.

Acid dichlorodiaquodiamminecobalt sulphate,

$$[Co(NH_3)_2(H_2O)_2Cl_2]SO_4H,$$

is obtained by adding the preceding potassium salt (3 grams) to a mixture of equal volumes of sulphuric and hydrochloric acids, cooled with ice and salt, and allowing the mixture to remain some hours in the freezing mixture. After 24 hours, the product is washed with alcohol and ether, dissolved in ice-cold water, and precipitated with sulphuric acid. It crystallises in lustrous, malachite-green needles, is easily

soluble in water, and yields a green solution which quickly changes to blue. The solution has an acid reaction.

Dichlorodiaquodiamminecobalt nitrate, $[Co(NH_3)_2(H_2O)_2Cl_2]NO_3$, is obtained by treating a cold solution of the preceding salt with concentrated nitric acid. It is a dark-green, crystalline powder, dissolves easily in water, forming a green solution which quickly becomes blue, and decomposes, when kept in a closed vessel, yielding an insoluble brown powder containing cobalt oxide. The *chloride*, $[Co(NH_3)_2(H_2O)_2Cl_2]Cl$, is obtained by treating the acid sulphate with hydrochloric acid. It is a malachite-green, crystalline powder easily soluble in water, yielding a green solution which changes to blue.

Chlorotriaquodiamminecobalt sulphate, $[Co(NH_3)_2(H_2O)_3Cl]SO_4 + H_2O$, is obtained by allowing a solution of the acid sulphate to remain at the ordinary temperature, and after adding a few drops of sulphuric acid, evaporating the solution in a vacuum over sulphuric acid. It separates in short, indigo-blue crystals, and is less soluble than the acid sulphate.

Isomeric dichlorodiaquodiamminecobalt chloride,

$$[Co(NH_3)_2(H_2O)_2Cl_2]Cl,$$

is obtained by treating the preceding salt with concentrated hydrochloric acid until all the sulphuric acid is eliminated. It is a green powder which dissolves easily in water when it at once gives a blue solution. E. C. R.

Fluidity of Fused Nickel. By JULES GARNIER (*Compt. rend.*, 1897, **124**, 1447—1448).—When fused at a high temperature, nickel is very mobile, and readily penetrates charcoal, forming, when cold, slender, hair-like filaments, very flexible and malleable. C. H. B.

Reduction of Molybdic Anhydride by Hydrogen. By M. GUICHARD (*Compt. rend.*, 1897, **125**, 26—29 and 105—106).—The statements of different chemists as to the products of the reduction of molybdic anhydride by hydrogen are very conflicting, and the author has therefore reinvestigated the reaction, special attention being directed to the possible production of oxides intermediate between the trioxide and the dioxide. The hydrogen was carefully purified and dried; the oxide was contained in a U-tube heated in a bath of melted tin. For temperatures above 500°, the oxide was placed in a dish in a straight tube surrounded by asbestos and placed in an iron gutter, the temperatures being measured by means of a thermoelectric couple.

Reduction begins at about 300°, the yellow colour changing to bluish-grey, but it is not rapid below 470°; the only product under these conditions is the dioxide MO_2, and examination of the residue at various stages of the reduction shows that no intermediate oxide is formed.

The dioxide begins to lose oxygen at about 500°, reduction becoming very distinct at 550°, and more rapid at 600°; the sole product is metallic molybdenum, the product of incomplete reduction at any stage being a mixture of the metal with the dioxide.

Contrary to the statement of Liechti and Kempe, molybdenum dioxide does not volatilise when heated in hydrogen chloride.

C. H. B.

Salts of Sulphomolybdic Acid. By ARTHUR ROSENHEIM (*Zeit. anorg. Chem.*, 1897, **15**, 180—191).—Since the author's previous communication (Abstr., 1895, ii, 18), Friedheim and Euler have published their iodometric method for the estimation of molybdic acid (Abstr., 1895, ii, 535), and on repeating the analyses of the salts previously described the author finds that his results were incorrect.

Action of Sulphurous Acid on Paramolybdates.—The sulphomolybdates are obtained by treating a saturated solution of the paramolybdate at the ordinary temperature with sulphurous anhydride; the potassium and sodium salts have been previously described. The cæsium and rubidium salts are very similar to the potassium salt, but the lithium salt could not be obtained pure, as it is more soluble than lithium sulphite, and on further concentration of the solution decomposition takes place. The salts have the following composition: $2Na_2O,2SO_2,5MO_3 + 8H_2O$; $2K_2O,2SO_2,5MO_3 + H_2O$; $2Rb_2O,2SO_2,5MO_3 + \frac{1}{2}H_2O$; $2Cs_2O,2SO_2,5MO_3 + 6H_2O$. They decompose if allowed to remain in the mother liquor for some time, the corresponding trimolybdate being precipitated; and, even when dry, they gradually decompose with evolution of sulphurous anhydride. When a dilute solution of ammonium paramolybdate is treated at the ordinary temperature with sulphurous anhydride, the salt $3(NH_4)_2O,2SO_2,8MO_3 + 5H_2O$ is formed; if, however, the solution is well cooled, a mixture of this salt with the *salt* $2(NH_4)_2O,2SO_2,5MO_3 + 12H_2O$ is obtained. The latter salt, which is obtained pure by adding a saturated solution of ammonium chloride to a freshly prepared concentrated solution of the sodium salt, crystallises in long, white needles, and very readily decomposes with evolution of sulphurous anhydride. Although the corresponding salts of the alkaline earths cannot be prepared by the action of sulphurous anhydride on the paramolybdates suspended in water, the *barium* and *strontium* salts are easily obtained by treating a freshly prepared solution of the sodium salt with the corresponding chlorides, and allowing the mixture to evaporate slowly over sulphuric acid; they crystallise in prismatic needles. The *calcium* salt, which crystallises in needles, cannot be obtained pure owing to its great solubility. Salts analogous to the stable ammonium salt, $3(NH_4)_2O,2SO_2,8MO_3 + 5H_2O$, cannot be prepared by double decomposition, for either the ammonium salt separates unchanged, or decomposition takes place with the formation of trimolybdates.

When normal molybdates, R_2O,MO_3, are treated with sulphurous anhydride in excess, the same salts are obtained as with the paramolybdates. If, however, the solution is not completely saturated with sulphurous anhydride, a mixture of sulphomolybdate and paramolybdate is obtained.

Action of Sulphurous Acid on Tetramolybdates.—When solutions of tetramolybdates, $R_2O,4MO_3$, are treated with sulphurous anhydride, octamolybdates, $R_2O,8MO_3$, are formed, but a sulphomolybdate could not be obtained. This is a very convenient method of preparing these salts. The potassium salt, $K_2O,8MO_3 + 13H_2O$, and the sodium salt, $Na_2O,8MO_3 + 15H_2O$, crystallise in well characterised prisms, the *ammonium* salt, with $13H_2O$ in lustrous, prismatic needles.

E. C. R.

Manganimolybdates. By E. PÉCHARD (*Compt. rend.*, 1897, **125**, 29—31).—When a solution of ammonium hydrogen molybdate is boiled with manganese peroxide, the liquid acquires a ruby-red colour, and when cooled deposits crystals of a new complex salt. Manganese peroxide prepared in various ways gives the same result, but the reaction is slow. A better method is to precipitate ammonium manganous molybdate by mixing solutions of the molybdate and a manganous salt; suspend this in water and add gradually a dilute solution of potassium permanganate. Another plan is to mix hot solutions of the molybdate and potassium permanganate, and reduce the latter by adding alcohol, aldehyde, &c. In both cases, the permanganate may be replaced by permanganic acid.

The *manganimolybdates* thus formed are readily crystallisable, red salts of the composition $3M'_2O,MnO_2,12MO_3$. They are stable at the ordinary temperature, but, when heated, decompose into manganese peroxide and an acid molybdate. Their solutions yield a precipitate of the peroxide when mixed with an acid or an alkali.

The ammonium salt contains $5H_2O$, and forms small, deep-red crystals slightly soluble in water; the potassium salt crystallises with $4H_2O$, is paler in colour than the ammonium salt, and is almost insoluble in water; the sodium salt crystallises with $13H_2O$ in large, efflorescent, blood-red crystals very soluble in water. The free acid obtained by the action of sulphuric acid on the barium salt does not crystallise, but when evaporated to dryness in a vacuum, forms a brilliant, black, amorphous mass with a vitreous fracture; it has the composition $MnO_2,12MO_3 + 10H_2O$, and its properties are similar to those of its salts.

Tungstic acid seems to yield no analogous compounds.

C. H. B.

Zirconotungstates. By L. A. HALLOPEAU (*Bull. Soc. Chim.*, 1896, [iii], **15**, 917—923).—*Potassium zirconodecatungstate*, $4K_2O,ZrO_2,10WO_3 + 15H_2O$, is prepared by dissolving gelatinous zirconia in a solution of potassium paratungstate with prolonged boiling. After filtration and concentration of the solution in a vacuum, it is obtained as a crystalline powder having a slight action on polarised light. From the mother liquor, on further concentration in a vacuum, *potassium dizirconodecatungstate*, $4K_2O,2ZrO_2,10WO_3 + 20H_2O$, is deposited; this forms very small, prismatic crystals, which act more powerfully on polarised light than those of the preceding compound, and lose $12H_2O$ at 100°. These substances are very slightly soluble in cold, but much more readily in hot water. They decompose on ignition, giving insoluble products, and, when fused with alkali carbonates are converted into a mixture of tungstate and zirconate, with abundant disengagement of carbonic anhydride. When the dizirconodecatungstate is heated to dull redness with an excess of sodium carbonate, the following reaction occurs:

$$4K_2O,2ZrO_2,10WO_3,20H_2O + 8Na_2CO_3 = 4K_2WO_4 + 6Na_2WO_4 + 2Na_2ZrO_3 + 8CO_2 + 20H_2O.$$

At a bright red heat, there is a further loss of carbonic anhydride.

Ammonium zirconodecatungstate, $3(NH_4)_2O,ZrO_2,10WO_3 + 13H_2O$, is

obtained in a similar manner to the corresponding potassium compound, substituting ammonium paratungstate for the potassium salt. It forms small, rhombic crystals, which act strongly on polarised light, and lose their water rapidly in the air, and slowly even in the liquid from which they have separated. Sometimes it separates in lenticular crystals either isolated or in tufts. This substance is very soluble in water, the solution having an acid reaction to litmus. The methods adopted by the author for the analysis of these compounds are similar to those employed by Marignac for the analysis of the analogous silicotungstates. The zirconodecatungstates are much more unstable than the silicodecatungstates, hydrochloric, sulphuric, and nitric acids immediately precipitating yellow tungstic acid from their solutions, whilst phosphoric acid slowly forms a gelatinous precipitate of zirconium phosphate. On adding ammonia to a solution of the acid ammonium salt described above, a precipitate of zirconia is formed which does not redissolve on expelling the excess of ammonia by boiling. The normal ammonium salt could not therefore be obtained. In this respect, the zirconodecatungstate behaves very differently from the corresponding silicodecatungstate. The chlorides of barium, calcium, and magnesium, and the nitrates of lead, silver, and mercury, give insoluble precipitates with solutions of the zirconodecatungstates.

Gelatinous zirconia does not dissolve in a solution of sodium paratungstate. A. C. C.

Thorium Compounds. By JOSEPH LESINSKY and CHARLES GUNDLICH (*Zeit. anorg. Chem.*, 1897, **15**, 81—83).—Thorium bromide, $ThBr_4 + 8H_2O$, is prepared in a pure state by dissolving pure thorium hydroxide, obtained by precipitating the nitrate with ammonia, in freshly distilled hydrobromic acid and evaporating the solution in the dark in a vacuum over sulphuric acid. The product, washed with light petroleum and chloroform, and recrystallised from alcohol, is obtained in large, white, hexagonal prisms, very easily soluble in alcohol and water. It melts at 100° in its water of crystallisation; a comparatively high temperature, however, is necessary to eliminate all the water.

The authors are engaged in the preparation of thorium iodide, chlorate, bromate, and iodate. E. C. R.

Potassium Sulphantimonites. By POUGET (*Compt. rend.*, 1897, **124**, 1445—1447).—The normal potassium sulphantimonite, K_3SbS_3, is obtained in small, white, very deliquescent crystals by dissolving antimony sulphide in a concentrated solution of the proper proportion of potassium sulphide, and rapidly concentrating the solution out of contact with air. The crystals are soluble in water, and alter rapidly when exposed to air.

The metasulphantimonite, $KSbS_2$, obtained by Ditte in the dry way, can also be prepared from a solution having the composition $Sb_2S_3 + 2K_2S + Aq$. If evaporated in a vacuum in the cold, this solution yields the compound $K_4Sb_2S_5$, but if heated out of contact with air, red, elongated octahedra of the salt $KSbS_2$ separate, whilst the normal sulphantimonite remains in solution. The red crystals are stable when exposed to air, and are insoluble in cold water, by which

they are only very slightly affected; they are, however, decomposed by boiling water, with separation of antimony sulphide.

C. H. B.

Preparation of Silver Sulphantimonites and Sulpharsenites by a Dry Method. By HERMANN SOMMERLAD (*Zeit. anorg. Chem.*, 1897, **15**, 173—179).—Artificial pyrargyrite, Ag_3SbS_3, is obtained by heating a dry mixture of silver chloride with antimony trisulphide in the proportion $3AgCl : Sb_2S_3$, in a retort from which the air has been driven out by carbonic anhydride. The reaction commences at 140°, and antimony trichloride distils over; the mixture is heated for some time at 360°, and then cautiously melted. The product is of a dark lead-colour with a reddish tinge, and has a radial fracture; it gives a dull-red streak, and a dark, cochineal-red powder. Under the microscope, in transmitted light, thin splinters are dark reddish-brown, whilst in reflected light they have a strong metallic lustre. The sp. gr. = 5·760 (the sp. gr. of natural pyrargyrite = 5·75—5·85). The chemical behaviour of the artificial compound agrees with that of the natural compound. When strongly heated in a glass tube, it yields a small sublimate of Sb_2O_3 and Sb_2S_3. The red powder is at first turned black by nitric and tartaric acids, and then dissolves with separation of sulphur, whilst with hydrochloric acid it is partially decomposed with evolution of hydrogen sulphide. Hot potassium hydroxide, ammonium sulphide, and potassium sulphide decompose the compound with precipitation of silver sulphide. It is not decomposed by ammonia.

Artificial miargyrite, $AgSbS_2$, is obtained in a similar manner by heating a mixture of silver chloride and antimony trisulphide in the proportion $3AgCl : 2Sb_2S_3$; the reaction commencing at 110°. The product is a lustrous black mass with a conchoidal fracture very similar to melted natural miargyrite. It gives a black streak, and a lustrous black powder. The sp. gr. = 5·200 (the sp. gr. of natural miargyrite = 5·184—5·4). The chemical behaviour of the compound agrees with that of the natural compound.

The author was unable to prepare artificial stephanite and polyargyrite by this method, although they are easily prepared by heating a mixture of their constituents.

Artificial proustite Ag_3AsS_3 is obtained by heating a mixture of silver chloride and arsenic sulphide in the proportion $3AgCl : As_2S_3$. The reaction commences at 150°, and the product is a brittle, reddish-black, lustrous mass having a radial fracture. It gives a bright red streak and powder, and under the microscope thin splinters appear bright reddish-brown. The sp. gr. = 5·49 (the sp. gr. of natural proustite = 5·5). The author has also prepared the compounds $AgAsS_2$ and $Ag_4As_2S_5$ by this method.

Artificial zinckenite, $PbSb_2S_4$, is obtained by heating a mixture of lead chloride and antimony sulphide.

E. C. R.

Silver Sulphantimonites. By POUGET (*Compt. rend.*, 1897, **124**, 1518—1520).—The products of the action of solutions of silver nitrate on solutions of potassium sulphantimonite (preceding page) vary with the concentration of the solutions, the proportions of the reacting substances, and the temperature. With dilute solutions and

an excess of the sulphantimonite, the product is an amorphous, black precipitate of normal silver sulphantimonite, Ag_3SbS_3. If, however, the solution contains not less than 0·29 of a gram-molecule of the sulphantimonite per litre, and only a small proportion of silver nitrate is added, the black precipitate is converted into a yellow, crystalline one of the composition Ag_2KSbS_3, and this conversion continues until the proportion of unaltered sulphantimonite left in the solution reaches the limit specified. This double sulphantimonite is at once converted into the normal silver salt by the action of silver nitrate. The double salt is also obtained by the action of excess of potassium sulphantimonite on silver sulphite; it is decomposed by alkali sulphides, with separation of silver sulphide, and when boiled with water, splits up into the normal potassium salt and the normal silver salt, the latter under these conditions being crystalline, lustrous, and reddish in colour.

When an excess of silver nitrate is added to the alkali sulphantimonite, the precipitate is always black, and contains more silver sulphide than corresponds with the formula Ag_3SbS_3, the reason being that silver nitrate partially decomposes the sulphantimonite, and the solution always contains some antimony precipitable by hydrogen sulphide. Silver nitrate solution, in fact, decomposes precipitated antimony sulphide, a mixture of silver and antimony sulphides being formed. All the silver is precipitated and antimony passes into solution. C. H. B.

Mineralogical Chemistry.

Platinum. By W. J. MARTIN, Junr. (*16th Ann. Rept. U.S. Geol. Survey*, for 1894–5, Pt. III, 1895, 628—633).—This paper contains the results of the mineralogical examinations of platinum from numerous localities; seventeen analyses are given of crude material, and nine of iridosmine obtained from crude platinum. No relation can be traced between the magnetic properties of the grains and the amount of iron shown in the analyses, some of the samples poorer in iron being more magnetic than those containing more iron. Samples from the same region differ widely in composition; for example, from Colombia, S.A., 38—90; Russia, 49—84 per cent. of platinum; Oregon, 24—94 per cent. of iridosmine. L. J. S.

Asphaltic Rocks and the Origin of Asphaltum. By STANISLAS MEUNIER (*Compt. rend.*, 1896, **123**, 1327—1329).—The asphaltum of bituminous rocks is completely dissolved out by digesting the powdered rock with carbon bisulphide; this affords a ready method for determining the amount of asphaltum present. A bituminous rock from Travers in Neuchâtel has been examined in this way. Numerous so-called bituminous rocks from various localities, including oil-shales, coals, &c., in which fossils are often present, were found to contain no asphaltum, there being nothing which could be dissolved out by carbon

bisulphide. Since, in the latter case, the carbonaceous matter is of organic (animal and vegetable) origin, it is concluded that true asphaltum is of deep seated origin, and is the result of purely mineral reactions of the type of the double decomposition of metallic carbides and water.

L. J. S.

Roumanite [Rumänite]. By CONSTANTIN I. ISTRATI (*Bul. Soc. Sci., Bucarest*, 1897, **6**, 55—59. Compare Abstr., 1894, ii, 457).—The amber-like resin, called roumanite, has been found in a bed of ozocerite, at Mosori, north of Tîrgu-Ocna, in Moldavia. It is of a yellow colour with a tinge of green, and in parts dark; it is hard and not friable, and has a conchoidal fracture; analyses gave the results under I. A black, bituminous variety from Buzĕŭ district, in Moldavia, contained C, 81·17; H, 13·28; sp. gr. = 0·9988, this being lower than that of other varieties (sp. gr. = 1·09—1·119). The other analyses of Moldavian roumanite are quoted from the author's previous papers (*Bul. Soc. Sci. Fizice*, 1895, **4**, 59—77; *Anal. Acad. Romåne*, 1895, **16**).

	C.	H.	O [diff.].	S.	Ash.
I. Yellow	83·319	10·659	3·88	1·72	0·4185
Blackish-yellow ...	77·79	10·76	9·98	1·29	0·18
Reddish	79·81	10·31	8·21	1·33	0·52
Blackish-yellow ...	81·28	10·48	6·13	1·47	0·64
Yellow	81·68	9·80	6·40	1·27	0·85
Black	83·29	10·77	4·45	0·93	0·56
Black, bituminous	81·17	10·39	6·63	1·10	1·00
Garnet red	82·07	11·11	5·20	0·93	0·69

L. J. S.

Ozocerite from Moldavia. By CONSTANTIN I. ISTRATI (*Bul. Soc. Sci., Bucarest*, 1897, **6**, 61—93).—An exhaustive account is given of Moldavian ozocerite. It occurs in beds $\frac{1}{4}$—$\frac{1}{3}$ metre thick in Miocene sandstone, and is of wide distribution. When first dug out, it is pale yellow and soft, like wax, but on long exposure to the air it becomes heavier, more compact, and darker in colour, then giving a greenish streak; these changes are due to the loss of volatile hydrocarbons. The original characters are retained in the interior of large specimens. Previous analyses are collected together, and several new ones added. The following varieties are distinguished:—

	C.	H.	Sp. gr.	Melting point.
Ozocerite proper	84 —86	13·5—14·5	0·85—0·93	61— 65·5°
Pietricikite	84 —85	14 —15	0·94—0·95	82— 90
Moldovite	84·5—85	14 —15	0·96—0·97	95—100

Moldovite is a new name for the variety from Mosori, north of Tîrgu-Ocna; it differs in appearance from the other varieties, and has a higher sp. gr. and melting point. *Pietricikite* is the correct spelling of Dana's zietrisikite.

L. J. S.

Marcasite, &c., Pseudomorphous after Pyrrhotite. By ALFRED LACROIX (*Compt. rend.*, 1897, **125**, 265—267).—The marcasite which occurs on the fibrous blende at Pontpéan mine, near Rennes, Dept. Ille-et-Vilaine, is described, and four types of crystals

distinguished. With it are hexagonal plates, which are pseudomorphs of marcasite, or of marcasite, pyrites, and galena after pyrrhotite. The crystals of these minerals are arranged in certain regular positions with respect to the pyrrhotite forms. L. J. S.

Bournonite from Isère. By PIERRE TERMIER (*Bull. Soc. fran. Min.*, 1897, **20**, 101—110).—Bournonite was formerly found with galena in a quartz and dolomite vein in a coal mine at Peychagnard, Isère. Analysis by Pisani of crystallised material gave

S.	Sb.	Pb.	Cu.	As.	Fe, Ag.	Total.
20·2	24·7	40·0	13·7	trace	nil	98·6

Sp. gr. = 5·78. A detailed description is given of two crystals, and six new forms are noted. L. J. S.

Sylvanite from Kalgoorlie. By AUGUST FRENZEL (*Tsch. Min. Mitth.*, 1897, **17**, 288—289).—Sylvanite occurs in schistose rocks in more than one mine in the auriferous district about Kalgoorlie, Hannan's district, Western Australia. It is silvery white with metallic lustre, and has a perfect cleavage in one direction. H = $2\frac{1}{2}$; sp. gr. = 8·14. The analysis agrees with the formula $(Au,Ag)Te_2$.

Te.	Au.	Ag.	Total.
58·63	36·60	3·82	99·05

An iron-black telluride of gold and silver with conchoidal fracture and no cleavage also occurs here. L. J. S.

[Scheelite, Tetradymite, Altaite, Stromeyerite, Danaite, &c., from Canada.] By G. CHRISTIAN HOFFMANN (*Rept. Geol. Survey, Canada*, 1897, **8** (1895), R, 1—59).—*Scheelite.*—Massive scheelite of a light smoke-grey colour occurs with mispickel and pyrites in a quartz vein in the Malaga gold mining district, Queen's Co., Nova Scotia. Analysis gave

WO_3.	CaO.	CO_2.	Insol.	Total.	Sp. gr.
79·01	19·80	0·71	0·11	99·63	6·002

Tetradymite.—This occurs with altaite and hessite near Liddel Creek in the West Kootenay district, British Columbia. It has a foliated structure, the colour being lead-grey to steel-grey. The streak is black. Analysis gave

Te.	S.	Se.	Bi.	Pb.	Ag.	Tl.	Insol. (quartz).	Total.	Sp. gr.
36·01	4·30	trace	51·85	3·50	0·91	trace	3·52	100·09	7·184

Deducting quartz, altaite, and hessite, this gives the formula

$$2Bi_2Te_3,Bi_2S_3.$$

Altaite.—Massive altaite occurs with hessite, gold, copper, &c., in a quartz vein at Long Lake, Yale district, British Columbia. It is tin-white, with sometimes a bronze-yellow tarnish. Analysis gave

Te.	Pb.	Ag.	Fe.	Au (free).	Insol. (quartz).	Total.	Sp. gr.
39·57	49·72	2·09	0·63	0·01	7·84	99·86	8·081

This corresponds with 87·46 per cent. of altaite, with some hessite, and apparently 8·24 per cent. of native tellurium. Analysis of the

associated hessite gave Te, 37·33; Ag, 60·68; Au, 2·29 = 100·30 per cent. Petzite, also from the Yale district, was found to contain 23·10 and 18·79 per cent. of gold.

Stromeyerite.—With bornite, chalcopyrite, galena, argentite, &c., from Toad Mtn., West Kootenay district, B.C. Massive, with subconchoidal fracture. Colour, dark steel-grey. Streak, dark grey and shining. Analysis gave

S.	Ag.	Cu.	Fe.	Total.	Sp. gr.
15·74	52·27	31·60	0·17	99·78	6·277

Danaite.—This occurs massive with pyrrhotite, mispickel, and pyrites at Monte Cristo Mtn., West Kootenay district, B.C. The colour is silver-white. Analysis gave

As.	S.	Fe.	Co.	Insol. (quartz).	Total.	Sp. gr.
46·41	19·21	28·91	2·97	3·86	101·36	6·166

The above analyses, in each case the mean of two, are by R. A. A. Johnston. The specific gravities given have been corrected for contained quartz. The report also includes analyses of limestones, dolomites, coals, iron ores, nickeliferous pyrrhotites, waters, &c., as well as numerous gold and silver assays. L. J. S.

[Coral Limestones from Florida.] By EDMUND OTIS HOVEY (*Bull. Mus. Comp. Zool. Harvard Coll.*, 1896, **28**, 63—91).—Several analyses, by G. Steiger, are given of coral limestones from the artesian well borings at Key West, Florida. The limestones have an oolitic structure, and contain particles of quartz sand.

L. J. S.

[Origin of Iron Ores.] By L. DE LAUNAY (*Compt. rend.*, 1897, **124**, 689—692; and *Ann. des Mines*, 1897, **12**, 178—185).—Large masses of iron carbonate have been supposed to have been deposited as such from water; the author, however, considers them to have been formed by the action of limestones on iron salts derived from iron sulphide. In support of this view, it is pointed out that, whilst deposits of iron sulphide always occur in schists, those of iron carbonate always occur in limestones. By the surface oxidation of the carbonate, deposits of oxides are formed. L. J. S.

A Mineral allied to Pinakiolite from Långban. By HELGE BÄCKSTRÖM (*Jahrb. f. Min.*, 1897, i, 243, Ref.; from *Geol. Fören. i Stockholm Förh.*, 1895, **17**, 257).—The mineral is found with hausmannite, a brownish arsenate, and sometimes pinakiolite, in the granular dolomite of Långban, Sweden; it is iron black with metallic lustre, and occurs in broken, striated prisms of rhombic outline with an angle of 68° $36\frac{1}{2}'$; the forms {120} and {210} are also present. There is no cleavage; sp. gr. = 3·935; H = 6. Very thin sections are transparent, and of a dark reddish-brown colour; the extinction is straight, and the c axis is the direction of greatest absorption. It is soluble in hydrochloric acid with evolution of chlorine. Analysis gave:

B_2O_3.	Fe_2O_3.	MnO.	O.	CaO.	PbO.	MgO.	SiO_2	Total.
13·92	10·52	46·95	3·45	1·35	1·22	22·36	0·78	100·55

This composition is like that of pinakiolite, but, although the mineral is orthorhombic, the crystallographic characters are different. More material is to be examined before a new name is given.

L. J. S.

Crystallised Mineral formed in Leaden Coffins. By ALFRED LACROIX (*Compt. rend.*, 1897, **124**, 419—422; and *Bull. Soc. fran. Min.*, 1897, **20**, 112—118).—Two leaden coffins, dated 1630, have recently been dug up in Paris; the contained skeletons are in part thinly incrusted with needles and plates of a substance which is referred to metabrushite ($H_2Ca_2P_2O_8 + 3\frac{1}{2}H_2O$). The white, acicular crystals are best developed in the interior of the skull, where they attain a length of 8 mm. Material, which, however, could not be completely separated from organic matter, lost 25·50 per cent. on ignition. The sp. gr. of the pure crystals is 2·31. The crystals are monosymmetric, and are flattened, and have a perfect cleavage, parallel to the plane of symmetry; the optic axial plane and obtuse bisectrix are perpendicular to the plane of symmetry; $2V_a = 81°$; optically negative. Some of these characters are in agreement with brushite ($H_2Ca_2P_2O_8 + 4H_2O$), so that the reference to metabrushite is not beyond doubt.

The mode of formation of this substance must have been the same as that described by Gautier (Abstr., 1893, ii, 536; 1896, ii, 185). Ammonium phosphate, produced by the decomposition of organic matter, especially the brain, acting on the calcium carbonate of the bones, would give rise to calcium phosphate. These reactions, taking place within the body itself, furnish a case of "automineralisation."

L. J. S.

Synthesis of Hanksite. By AUGUST BENJAMIN DE SCHULTEN (*Compt. rend.*, 1896, **123**, 1325—1327).—When a hot solution of caustic soda (50 grams in 90 c.c. water) is poured into a hot solution of sodium sulphate and carbonate (20 grams $Na_2SO_4,10Aq$ and 0·8 gram Na_2CO_3 in 30 c.c. water), a crystalline precipitate, having the properties of natural hanksite, is formed; the crystals are freed from caustic soda by washing with alcohol. Unless these details are followed, thenardite is also formed. The analyses of the crystals, which are of sp. gr. 2·613, agree closely with the formula originally given for the natural mineral, namely, $4Na_2SO_4,Na_2CO_3$, and not with that recently proposed by Pratt (this vol., ii, 49). The crystals are hexagonal prisms measuring 0·05 × 0·03 mm., with the forms $c\{111\}$, $m\{2\bar{1}\bar{1}\}$, and sometimes $r\{100\}$ and $p\{13.1.1\}$. They are optically negative, and show optical anomalies; viewed in parallel polarised light through the basal plane, 6 or 12 sectors are seen, and through the prism planes 4 sectors. When crystals are slowly grown from a cold solution, no optical anomalies make their appearance; such crystals may be easily formed by allowing a concentrated solution of sodium sulphate and carbonate, with less caustic soda than in the previous case, to evaporate on a microscope slide.

L. J. S.

Isometric Crystals of Silica. By KONSTANTIN VON CHRUSTSCHOFF (*Jahrb. f. Min.*, 1897, i, 240 Ref.; from *Bull. Acad. Sci. St. Pétersbourg*, 1895, [v], **2**, 27—33).—An aqueous solution of silica, with a little

hydrogen borofluoride to act as a mineraliser, was heated for 5 hours in a sealed platinum vessel with the following results.

1.	At 180°	(= 10 atmos.).	No change.
2.	,, 180—228°	(= 26 atmos.).	Isometric crystals.
3.	,, 228—235°	(= 30 ,,).	No quartz.
4.	,, 240—300°	(= 86 ,,).	Quartz.
5.	,, 310—360°	(= 189 ,,).	Tridymite and some quartz.

The colourless transparent, isometric crystals show the forms $o\{111\}$, $a\{100\}$, and $d\{110\}$ in various combinations, and are twinned on the spinel law. They are perfectly isotropic, and have an index of refraction of about 1·58. Sp. gr. = 2·412. They are soluble in hydrofluoric acid; analysis gave 99·78 per cent. SiO_2. The crystals most resemble cristobalite, which is isotropic at 170°. L. J. S.

Formation of Zeolites. By Alfred Lacroix (*Compt. rend.*, 1896, **123**, 761—764).—Owing to the frequent occurrence of zeolites in volcanic rocks, it was formerly supposed that an elevated temperature was necessary for their production. But Daubrée and Bouis have described the formation of numerous zeolites by the action of hot springs having a temperature considerably below 100°; and phillipsite has been found in the deep-sea dredgings of the *Challenger*. Further, in the Pyrénées, zeolites are found in mineral veins, and in plutonic and sedimentary rocks. The present paper describes the formation of zeolites by the action of almost pure water, at the temperature of melting snow, on basic felspathic rocks.

In several elevated districts in the Pyrénées, in the beds of streams, or where the shattered and decomposed rocks are exposed to the action of running water derived from the melting of the snow, zeolites (chabazite, stilbite, and laumontite) are abundant, impregnating the rocks, or coating surfaces and cementing together fragments. These alterations take place in rocks, both plutonic and metamorphic, which contain basic plagioclases and dipyre, these minerals affording the necessary material for the formation of lime and soda-lime zeolites.

L. J. S.

Beryl in a Pseudomorph after Beryl. By Arvid G. Högbom (*Jahrb. f. Min.*, 1897, i, 431, Ref.; from *Geol. Fören. i Stockholm Förh.*, 1895, **17**, 412—414).—A large hexagonal prism, which was probably originally a crystal of beryl, consists of an irregular aggregate of beryl crystals with some chlorite, kaolin, and perhaps muscovite; in cavities, there are well developed crystals of beryl, the larger of a straw-yellow colour and the smaller water-clear. In these crystals, there are elongated cavities containing two liquids (one of which is probably carbonic anhydride), and bubbles of gas. Analysis of the beryl by G. Lundell gave

SiO_2.	Al_2O_3.	Fe_2O_3.	BeO.	CaO.	MgO.	Alkalis.	Loss on ignition.	Total.
65·14	21·72	trace	11·55	0·32	0·30	trace	1·64	100·67

Sp. gr. = 2·6. The loss on ignition is mostly due to the fluid enclosures. It seems that here the original beryl material has been altered and beryl again formed. L. J. S.

Edingtonite from Böhlet, Sweden. By GUSTAF LINDSTRÖM (*Öfvers. k. Vetensk.-Akad. Förh. Stockholm*, 1896, **53**, 469—472. Compare this vol., ii, 328).—The following analysis (I) is given of the edingtonite crystals recently found at the manganese mines of Böhlet, Vestergöthland; sp. gr. 2·782. Under II, is the analysis published by Heddle in 1855 of the Scotch mineral.

	SiO_2.	Al_2O_3.	Fe_2O_3.	BaO.	CaO.	MnO,MgO.	Na_2O.	K_2O.	H_2O.	Total.
I.	36·37	20·06	0·04	29·99	0·16	0·06	0·20	0·21	13·12	100·21
II.	36·98	22·63	—	26·84	trace	—	trace	—	12·46	98·91

Anal. I gives the ratios, Al_2O_3 : BaO(CaO and alkalis) : SiO_2 : H_2O = 1 : 1·04 : 3·06 : 3·70. A trace of chlorine is present, but no fluorine, strontium, or lithium. Most of the 0·06 per cent. of MnO,MgO is due to enclosed manganese ore; the pure mineral contains only a trace of magnesium, and neither iron nor manganese. At 100°, there is a loss of 3·82; at 155°, of 5·90, and at 230°, of 7·90 per cent.; if the mineral has not been too strongly heated, this water is reabsorbed with decrepitation, the material being transformed into a woolly mass consisting of fine needles. A second determination of the total water gave 13·08 per cent. L. J. S.

Constitution of Analcite. By CHARLES LEPIERRE (*Bull. Soc. Chim.*, 1896, [iii], **15**, 561—565).—Analcite, differing from the ordinary mineral in optical properties and crystalline form (as determined by Bensaude), gave the following results on analysis.

SiO_2.	Al_2O_3.	CaO.	Na_2O.	H_2O.	Total.
54·29	23·30	0·31	13·84	8·36	100·10

This agrees closely with the usual formula, $Na_2O,Al_2O_3,4SiO_2 + 2H_2O$. The mineral was free from calcite, and titanium and potassium were absent. About half (3·90 per cent.) of the water is lost at 200°, the remainder being expelled at 440°; over sulphuric acid, or at 100°, there is no loss. To express the difference in the behaviour of the two molecules of water, a structural formula is given, the mineral being considered as a salt of diorthosilicic acid, $H_6Si_2O_7$. This formula is simpler than that recently proposed by Clarke (Abstr., 1894, ii, 459). L. J. S.

[**Analysis of Ilvaite.**] By K. H. SCHNERR (*Jahrb. f. Min.*, 1897, i, 432 Ref.; from *Inaug.-Diss. München*, 1894. Compare this vol., ii, 106, 147).—The methods employed in the analysis of several garnets are described in detail in the dissertation (but not in the abstract quoted), especially the estimation of ferrous and ferric iron by decomposing the mineral with potassium iodide and sulphuric acid, and then volumetrically determining the separated iodine. This method was tested on ilvaite (of which the complete analysis is given below) and magnetite.

SiO_2.	FeO.	Fe_2O_3.	MnO.	CaO.	H_2O.	Total.
29·42	34·13	21·29	0·30	13·41	1·71	100·19.

L. J. S.

Fayalite. By GEORGE OTIS SMITH (*Johns Hopkins Univ. Circulars*, 1894, **13**, 82).—Fayalite, in perfect skeleton crystals of tabular habit, from the surface of a crystallised iron slag, gave $a : b : c =$

0·4632 : 1 : 0·5835. An analysis of the crystals, by T. L. Blalock, agrees with the formula Fe_2SiO_4.

SiO_2.	FeO	CaO.	MgO.	Total.
30·10	68·43	0·57	0·13	99·23

L. J. S.

Action of Volcanic Fumaroles on Serpentine. By ALFRED LACROIX (*Compt. rend.*, 1897, **124**, 513—516).—In the ravine of Sasaki, near Kalamaki in the Gulf of Corinth, serpentine is overlain by Pliocene limestones; and at the contact between these are volcanic fumaroles which give off water vapour charged with hydrogen sulphide and carbonic anhydride. The limestone is converted into gypsum; and the serpentine, by the elimination of magnesium and iron in the form of epsomite and melanterite, is finally converted into opal or quartz and chalcedony. This opal preserves the original minute structure of the rock, and in it the original grains of picotite are sometimes embedded. The less completely altered rock contains epsomite, melanterite, marcasite and native sulphur, and, as secondary products derived from the marcasite, various basic ferric sulphates. The acid rocks (rhyolites, &c.) of the same district are reduced by solfataric action to the same end-product, here, however, with the production of various aluminium and alkali sulphates. L. J. S.

[Chrome-diopside, Hornblende and Pleonaste from Montana.] By GEORGE P. MERRILL (*Proc. U.S. National Museum*, 1895, **17**, (1894), 637—673).—In a paper describing a collection of eruptive rocks from Gallatin, Jefferson, and Madison Counties, Montana, the following mineral analyses are given.

Augite, in small green crystals from a rock related to olivine-basalt near Bozeman, gave analysis I (by L. G. Eakins) showing it to be a chrome-diopside. Dark green hornblende, which, with hypersthene, forms pyroxenite between Meadow and Granite Creeks, gave II. Dark green pleonaste, occurring abundantly in a similar pyroxenite, gave III (Eakins); sp. gr. 3·89.

	SiO_2.	Cr_2O_3.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	MgO.	K_2O.	Na_2O.	H_2O.	Total.
I.	52·50	1·07	2·26	2·05	2·47	trace	21·70	17·11	0·07	0·35	0·64	100·22
II.	46·14	—	17·07	8·45	not det.	—	11·70	15·01	0·10	1·11	—	99·58
III.	0·55	2·62	62·09	2·10	17·56	trace	0·16	15·61	—	—	—	100·69

L. J. S.

Jadeite from "Tibet." By MAX BAUER (*Jahrb. f. Min.*, 1897, i, 258—259. Compare Abstr., 1896, ii, 310).—The presence of nephelite in the jadeite from "Tibet," described in the previous paper (*loc. cit.*), suggested that nephelite might be a constituent of crystalline schists as well as of igneous rocks; this is now confirmed by the presence of some chlorite-schist on one of the new specimens examined by the author. Chemical and optical tests of this chlorite were made. L. J. S.

[Augite from Madras.] By THOMAS H. HOLLAND (*Quart. Journ. Geol. Soc.*, 1897, **53**, 405—419).—In a petrological paper, the following analysis (I) is given of pale brown augite, which, with a plagioclase near labradorite, and a ground-mass of micropegmatite, forms an augite-diorite dyke at the Seven Pagodas, Chingelput district, Madras Presidency. The bulk analysis of the rock is given under II.

	SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	MgO.	Na_2O.	K_2O.	H_2O.	P_2O_5.	Total.
I.	50·02	—	5·61	15·61	—	trace	14·84	12·01	0·96		0·76	—	99·81
II.	51·15	0·44	15·92	9·34	2·87	0·09	10·40	6·48	1·19	1·61	0·11	0·06	99·66

L. J. S.

American Kaolins. By CHARLES FREDERIC MABERY and OTIS T. KLOOZ (*Journ. Amer. Chem. Soc.*, 1896, **18**, 909—915).—Eleven analyses are given of American pottery clays; these are compared with the best German and English china clays. They all contain free silica, 1·33—80·30 per cent. The purest kaolin, from Woodbridge, Middlesex Co., N.J., gave

SiO_2.	Al_2O_3.	Iron.	CaO.	MgO.	K_2O.	Na_2O.	Combined H_2O.
44·34	38·09	0·15	0·96	0·10	1·00	0·79	14·34

L. J. S.

Meteoric Iron. By EMIL W. COHEN (*Jahrb. f. Min.*, 1897, i, 254—255 Ref.; from *Ann. k.k. naturhist. Hofmuseums*, 1895, **10**, 81—93).—In No. IV. of his "Meteoric Iron Studies," the author gives the results of the examination of the magnetic characters and specific gravity of numerous irons.

Most irons may easily be strongly permanently magnetised; when this is not the case, the iron has been heated and slowly cooled. All irons, when strongly heated and quickly cooled, become magnetic, and this magnetism is retained for some time. Tænite behaves as meteoric iron, but cohenite and schreibersite are rather less easily magnetised.

In general, irons having the same chemical composition have much the same specific gravity; and the specific gravities calculated from the composition do not vary much from the observed values. Hexahedral iron has an average sp. gr. of 7·80—7·88, and in octahedral iron the sp. gr. varies from 7·78 to 7·86, being greater when the lamellæ are finer, and when more nickel is present. L. J. S.

River Waters of Bohemia. By JOSEPH HANAMANN (*Jahrb. f. Min.*, 1897, i, 289—291 Ref.; from *Archiv naturw. Landes. Böhmen*, 1894, **9**, No. 4, 102 pp.).—Numerous analyses are given of the waters of the River Eger and its tributaries. These show the variation in the mineral constituents of waters collected from different geological formations, for example, from phyllites, granites, basalts, &c. Analyses of water, taken from several points between the source and the mouth of the river, show that almost all the bases and acids, with the exception of silica, increase in amount towards the mouth. The total solids vary at different seasons of the year. The composition of the water of the Eger is compared with that of other rivers. L. J. S.

Water from Wells in the Nubian Desert. By EMILY A. ASTON (*Quart. Journ. Geol. Soc.*, 1897, **53**, 374—375).—As an appendix to a paper by H. G. Lyons on the geology of a portion of the Nubian Desert, the following analyses are given of water from the wells sunk in the sand-and-gravel detritus of the Desert. I, Murrat Wells. II, Bir Tilat Abda, called by the Arabs a 'bitter' well. III, Bir Ab Araga.

	SiO_2.	$Fe_2O_3+Al_2O_3$.	Ca.	Mg.	Na.	K.	SO_4.	Cl.	NO_3.	Total.
I.	1·28	0·26	37·76	5·81	61·38	32·08	175·23	61·79	1·86	377·45
II.	3·36	4·36	31·19	6·74	63·88	30·41	182·52	21·42	1·88	345·76
III.	2·48	0·96	37·95	6·89	21·91	11·18	142·47	28·05	trace	251·89

'Total solid matter' found by direct evaporation, 410·5, 359·5, 253·5; $CaCO_3,H_2CO_3$, 82·04, 28·79, 10·56 respectively. The above results are in grains per gallon. Free ammonia, 0·378, 0·105, 0·199; albuminoid ammonia, 0·185, 0·173, 0·260, respectively, in parts per million. L. J. S.

Mineral Water from Pennsylvania. By A. E. Robinson and Charles Frederic Mabery (*Journ. Amer. Chem. Soc.*, 1896, **18**, 915—918).—Mineral springs having therapeutic qualities occur in the north-western portion of Pennsylvania; the following analyses are of waters from Conneautville, in Crawford Co. Water from surface springs at this place, which are representative of the springs of the region, gave, in grains per gallon; K_2CO_3, 0·985; Li_2CO_3, 0·002; NaCl, 0·925; $CaH_2(CO_3)_2$, 2·879; $CaSO_4$, 1·291; $MgCl_2$, 0·204; $FeCO_3$, 0·743; SiO_2, 0·233; H_2S, trace; total solids, 6·586. Sp. gr., 1·0002 at 20°.

Bittern water from a boring 2,667 feet in depth gave, in parts per 100,000: KCl, 755·6; LiCl, 80·3; AmCl, 216·6; NaCl, 14,430·0; KBr, 245·7; KI, 2·96; $MgCl_2$, 3096·0; $CaCl_2$, 11,880·0; $CaSO_4$, 11·1; $FeCO_3$, 163·5; $AlCl_3$, 31·1; SiO_2, 4·6; H_2S, 0·05; total solids, 30,536. Sp. gr., 1·205 at 15°. This water is remarkable on account of the presence of large amounts of ammonium chloride, potassium iodide, and lithium. Cæsium and rubidium are absent. L. J. S.

Physiological Chemistry.

Action of Albumoses and Peptones in Intravascular Injections. By EDMOND FIQUET (*Compt. rend.*, 1897, **124**, 1371—1374).—Peptones prepared in the usual way were dissolved in a small quantity of water, the albumins, albumoses, and albumotoxins precipitated by ammonium sulphate, and alcohol added until the alcoholic strength of the liquid was 68—70°. The filtrate was then concentrated, dialysed, and the peptones precipitated by strong alcohol.

Albumoses, prepared by the action of pancreatic juice on beef, were purified by first adding to their concentrated solution sufficient alcohol to bring its strength up to 50°, and then mixing the filtrate with a further quantity of alcohol to bring its strength up to 66—88°, when the albumoses were precipitated.

The albumoses and peptones thus purified were injected into dogs and rabbits in quantities amounting in some cases to as much as 7·7 grams per kilogram of body weight at one injection, whilst in others the injections were repeated on several successive days. No injurious effects were observed; the coagulation of the blood was not prevented and there was neither narcosis nor tremors. The author

concludes that the poisonous effects generally attributed to albumoses and peptones are really due to albumotoxins, ptomaines, &c., which have not been completely removed in the process of purification.

C. H. B.

Behaviour of some Varieties of Sugar in the Animal Organism. By FRITZ VOIT (*Bied. Centr.*, 1897, **26**, 384—385; from *Neue Zeits. Zuckerind.*, 1896, 309).—Dextrose and levulose are both sugars which produce glycogen; whether galactose belongs to the group is doubtful, but, in any case, it is much less favourable to the production of glycogen than are dextrose and levulose. Formation of glycogen from di- and poly-saccharides depends on their behaviour in the intestinal canal, where they are decomposed into simple sugars which may, or may not, belong to the class which yields glycogen.

Cane-sugar is inverted, in the intestinal canal, into dextrose and levulose from which glycogen is produced. Maltose behaves similarly, whilst the behaviour of lactose is not yet established.

The migration of the various sugars to the urine also depends on the fermentability and production of glycogens. Whilst grape-sugar, which ferments readily, must be consumed in large quantity to show sugar in the urine, a separation of sugar takes place after very small doses of sorbose, which does not ferment.

Experiments with animals, in which sugars were injected subcutaneously, showed that dextrose and levulose produced glycogen, whilst with cane-sugar and lactose there was only a slight formation of glycogen. Further experiments showed that dextrose, levulose, and galactose did not appear in human urine, being rapidly decomposed in the organism. When the disaccharides, saccharose, and lactose were injected, the whole amount was recovered in the urine, whilst maltose disappeared. It is supposed that maltose is either attacked by the cells, or else that it is converted, in the liver, into glycogen either directly or indirectly.

N. H. J. M.

Composition of Milk and Milk Products. By HENRY DROOP RICHMOND (*Analyst*, **22**, 1897, 93—95).—The author gives the average composition of 11,633 samples of milk taken from railway churns on arrival at the depôts of the Aylesbury Dairy Co. during 1896.

The results again show that the non-fatty solids are fairly constant, varying from 8·7 to 9·1 per cent. In a few instances, they were as low as 7·5 to 8·4 per cent., but in such abnormal milks, which are rarely met with, the ash is much higher than would have been the case if the deficiency in non-fatty solids had been caused by watering. The lowest fat recorded is 3·40 per cent.

Analyses of cream and butter are also given. L. DE K.

Colostrum Fat. By ROBERT EICHLOFF (*Bied. Centr.*, 1897, **26**, 385—386; from *Milchztg.*, 1897, No. 5, 67).—The fat was separated in the following manner:—The colostrum was well mixed with water (3 parts), left for eighteen hours, and the creamy layer removed. This was kept at 4°, for 8 hours, and churned for 35 minutes, after which the butter was washed as usual. The butter was of a deep golden colour, of almost waxy consistency, had an unpleasant odour and taste,

and melted at 35°. In composition, it resembled ordinary butter except that the percentage of proteids (1·71) was higher, and the percentage of ash (0·05) lower. By fractional separation with ether, the fat was separated into a white, crystalline mass, comparatively sparingly soluble in ether, and a readily soluble, dark yellow oil, the colouring matter of which the author supposes to be identical with that of urine.

The yield of fat was 70 per cent. of the colostrum. Sp. gr. = 0·8648—0·8665; melting point = 37·6. N. H. J. M.

Analysis of Urine: Thermo-optically Positive and Negative Diabetic Sugar. By FRÉDÉRIC LANDOLPH (*Compt. rend.*, 1897, **125**, 118—119).—Diabetic urine ferments with great rapidity even at the ordinary, or lower, temperatures, and this is characteristic of the true diabetic sugar, the reducing power of which is double that of glucose. This sugar is thermo-optically positive, and when its solution is boiled, the rotatory power is increased, often by several degrees. The quantity of sugar corresponding with the result obtained by fermentation is generally in agreement with that indicated by the polaristrobometer, but the results with Fehling's solution are too high, and are variable and misleading. The cuprous oxide reduced by diabetic sugar differs both in colour and physical condition from that reduced by ordinary glucose.

Diabetic sugar is always accompanied by a certain quantity of a thermo-optically negative sugar, which, like glucose, partially or completely loses its positive rotatory power when its solution is boiled. It ferments much more slowly than the diabetic sugar, but is not identical with glucose; it generally precedes diabetes. C. H. B.

Formation of Hippuric Acid in the Animal Organism. By F. W THEODOR C. PFEIFFER and WILHELM EBER (*Landw. Versuchs-Stat.*, 1897, **49**, 97—144).—The results of previous experiments indicated the probable relation between pentoses consumed in food and the formation of hippuric acid (Abstr., 1896, ii, 443).

In the experiments now described, a horse was fed with ordinary food (clover and meadow hay, oats and salt), both alone, and in conjunction with quinine hydrochloride (10 and 20 grams), calomel (3 and 5 grams), and pentoses (500 grams of cherry gum) respectively; during one period the horse was rubbed with mustard spirit (5 per cent., 100 grams per day). During the experiment, which lasted about three and a half months, the amount of water consumed was recorded, and the amount of urine, its sp. gr., the amounts of nitrogen, hippuric acid, sulphuric acid, ethylsulphuric acid, and phosphoric acid were determined each day.

The results of the experiments point to the following conclusions. The decomposition of proteids cannot be the only source of the non-nitrogenous constituents of hippuric acid, whilst the resorbed pentoses have considerable effect in the production of hippuric acid. Interrupted formation of hippuric acid must be attributed either to a reduction of certain hitherto unknown processes of decomposition in the intestines (connected, possibly, with the digestion of cellulose), or else to metabolic processes subsequent to resorption in the intestines.

The pentoses of cherry gum were almost completely digested; this

agrees with the observations of Götze and Pfeiffer (*loc. cit.*) in experiments with sheep. N. H. J. M.

Chemistry of Vegetable Physiology and Agriculture.

Fermentation in Solid Materials. By TH. SCHLOESING, Junr. (*Compt. rend.*, 1897, **125**, 40—43).—In the case of fermentations in solid materials such as soil, farmyard manure, tobacco, and the like, it is commonly observed that the rate of fermentation first increases, then diminishes, and finally the change almost ceases, although the fermentable material is by no means exhausted. If, however, the material is well agitated and broken up, fermentation begins again and the same series of phenomena is observed, and this may be repeated several times.

Examination of the air in contact with the material shows that the cessation of activity is not due to absence of oxygen. Further, if all the gas is pumped out of the material and its pores, and fresh air is admitted, the effect, without agitation and breaking up, is almost *nil*, whilst, on the other hand, agitation has a marked effect on the activity of some anærobic fermentations. It would seem, therefore, that the renewed activity of the ferment is due to the mechanical disturbance and not to aëration, but exactly how the disturbance acts has yet to be ascertained. C. H. B.

Formation of Diastase. By WILHELM PFEFFER (*Bied. Centr.*, 1897, **26**, 400—401; from *Ber. Mathem.-phys. Klasse kgl. Sächs. Gesel. Wissens. Leipzig*).—*Penicillium glaucum*, *Aspergillus niger*, and *Bacterium megatherium* were cultivated in liquid media containing the necessary mineral matter, ammonium nitrate, and more or less sugar or other carbon compounds; starch was employed to detect diastase. It was found that the production of diastase diminished with increased amounts of sugar; in the case of *Penicillium glaucum*, diastase ceased to be formed in presence of 15 or 10 per cent. of cane-sugar, and even with 1·5 per cent. the starch was only slightly attacked. Similar results were obtained with *Bacterium megatherium*, whilst *Aspergillus niger* produced diastase even in presence of 30 per cent. of cane-sugar, although in diminished quantity.

With regard to the effect of different sugars in checking the formation of diastase, cane-sugar and dextrose were the most active, maltose less active.

Quinic acid (3—10 per cent.), glycerol, and tartaric acid were without any conspicuous effect on cultivations of *Penicillium glaucum*, and *Aspergillus niger.*

In cultivations containing peptone, instead of ammonium nitrate, greater amounts of sugar are required to check the production of diastase. N. H. J. M.

Oxidising Action of Manganese Salts: Constitution of Oxydases. By GABRIEL BERTRAND (*Compt. rend.*, 1897, 1355—1358).—See this vol., ii, 493.

Action of Guaiacol on the Germination of Spores of Aspergillus fumigatus. By EM. BOULANGER-DAUSSE (*J. Pharm.*, 1897, [vi], 5, 332—335 and 386—388).—The spores were sown on a sterilised slice of carrot covered with water, or in Raulin's liquid; in the former case, when 7 c.c. of distilled water was present, an addition of 4—5 drops of a 5 per cent. solution of guaiacol in glycerol was capable of preventing all traces of development. In the second series of experiments, when 7 c.c. of Raulin's liquid was used, the addition of 3—4 drops of the same antiseptic solution prevented germination.

J. J. S.

Composition of Haricots, Lentils, and Peas. By BALLAND (*Compt. rend.*, 1897, 125, 119—121).—The following results were obtained :—

	Haricots.		Lentils.		Peas.	
	Minimum.	Maximum.	Minimum.	Maximum.	Minimum.	Maximum.
Water	10·00	20·40	11·70	13·50	10·60	14·20
Nitrogen compounds	13·81	25·16	20·32	24·24	18·88	23·48
Fats	0·98	2·46	0·58	1·45	1·22	1·40
Sugars and starches	52·91	60·98	56·07	62·45	56·21	61·10
Cellulose	2·46	4·62	2·96	3·56	2·90	5·52
Ash	2·38	4·20	1·99	2·66	2·26	3·50

The minimum of nitrogen compounds and maximum of fats in the case of haricots are found only in very large Spanish haricots; with all other varieties, the variations are smaller and are similar to those obtained with peas and lentils. The germs, as in the case of beans, contain a high proportion of nitrogen compounds and very little fat. Egyptian lentils are the richest in nitrogen, and, as a rule, the small varieties of lentils are richer in nitrogen than the large ones. Peas, as Poggiale pointed out, contain the highest proportion of nitrogen before they have reached maturity. Haricots, lentils, and peas have the same acidity as beans; they lose only from 7 to 9 per cent. by decortication; and they undergo no change in chemical composition, even when kept for a long time, although the proportion of water that they will absorb, which at first is about 100 per cent. of their weight, diminishes with their age.

C. H. B.

Composition of Potatoes. By H. COUDON and L. BUSSARD (*Compt. rend.*, 1897, 125, 43—46).—The potato, after the skin has been removed, consists of three distinct layers, which differ in composition, namely, the cortical layer, the external medullary layer, and the internal medullary layer. The first contains the highest proportion of starch and the lowest proportion of water and nitrogenous matter, the last contains the highest proportion of nitrogenous matter and water and the lowest proportion of starch, whilst the middle layer is intermediate in composition. The proportion of starch in the cortical layer may be twice as great as in the innermost layer, whilst the quantity of nitrogenous matter in the innermost layer may be 28 per cent. more than in the cortical layer, the exact differences varying with the variety of potato.

The culinary value of potatoes is directly proportional to the quantity of nitrogenous compounds and inversely proportional to the quantity of starch that they contain, and may be measured by the ratio between these quantities, the ratio being from 17 to 25 for the best tubers in 1895 and below 8 for the worst. The tendency of the tubers to retain their shape and size when boiled in water, instead of swelling up and becoming floury, is not dependent on the proportion of starch or the size of the starch grains, or on the presence of pectic substances, but is determined by the proteids present. The resistance is greater the higher the proportion of proteids, and is measured by the ratio proteids/starch, the value of this ratio being 14·0 to 8·6 in the most resistant varieties, and from 8·0 to 6·6, or even as low as 4·3, in the varieties that disintegrate most readily.

It follows that, for table purposes, the aim should be to cultivate varieties low in starch and with a thin cortical layer, whilst for industrial purposes, a thick cortical layer and a high percentage of starch are desirable. C. H. B.

Effect of Manuring Peaty Meadows on the Amount of Water, Potash, and Phosphoric Acid in the Crops. By H. A. Moritz Fleischer (*Bied. Centr.*, 1897, **26**, 443—447; from *Mitteil. Ver. Förd. Moorkultur.*, 1896, No. 24, 453—462; 1897, No. 7, 129—139).—Application of kainite and phosphates to peaty soil raised the amount of water in the crop by 6 per cent. (average of 4 years). When potash alone was applied, the amount of water in the crop was scarcely changed, and similar results were obtained by the exclusive application of phosphates. The increase in the amount of water is ascribed to increased growth of leguminous herbage, and of varieties of grasses containing more water, in the place of drier grasses, and also to increase in the size of leaves, by which evaporation, and the taking up of water, would be increased. As regards the effect of potash and phosphate manuring on the amounts of these constituents in hay, as compared with the amounts in unmanured hay, the results varied according to the soil. On heavy soil, the percentages were raised as follows:—K_2O, 0·32; P_2O_5, 0·35 per cent.; on medium soil, the rise was $K_2O = 0·53$, $P_2O_5 = 0·30$ per cent.; on light soil, $K_2O = 0·89$, $P_2O_5 = 0·23$ per cent. In the Rothamsted grass experiments (*Jour. Roy. Agr. Soc. Eng.*, 1858, **19**, 552; 1859, **20**, 228 and 398), the percentage of potash in hay was raised from 1·20 to 1·94 per cent., the percentage of phosphoric acid from 0·29 to 0·44, under the influence of mineral manure including potash and phosphates.

Exclusive application of potash manure increased the percentage of potash in hay from 1·15 to 2·22 per cent., whilst the exclusive application of phosphates lowered the percentage of potash to 1·08. With both manures together, the percentage of potash in the hay did not rise above 1·71.

Phosphatic manure alone increased the percentage of phosphoric acid in the hay from 0·48 to 0·84 per cent.; potash manure alone lowered the percentage to 0·40. With potash and phosphates together, the highest percentage of phosphoric acid in the hay was 0·81.

N. H. J. M.

Analytical Chemistry.

Estimation of Carbonic Anhydride in Atmospheric Air, and the Dissociation of Sodium Hydrogen Carbonate. By ISIDOR ROSENTHAL (*Chem. Centr.*, 1896, i, 1142—1143; from *Sitz.-Ber. Phys. Med. Soc. Erlangen*, **27**, 74—84).—The principle of the method is the measurement of the volume of air required to remove the colour of 20 c.c. of N/1000 soda solution mixed with phenolphthalein. The apparatus is not fully described, but seems to resemble that of Schulz (Abstr., 1892, 533), with the addition of an inclined mirror and the exclusion of side light, by which means the moment of decolorisation is more exactly observed. When the proportion of carbonic anhydride is somewhat above the normal, the decolorisation is sharp, but with 0·04 per cent., the tension of dissociation of the sodium hydrogen carbonate exceeds the partial pressure of the carbonic anhydride in the air, so that complete decolorisation does not occur, and a tint remains which can be imitated by a highly dilute solution of carmine. Such a solution serves, therefore, as a standard. M. J. S.

Apparatus for Estimating Sulphur in Coal-Gas. By FERDINAND FISCHER (*Zeit. angw. Chem.*, 1897, 302—303).—Fifty litres of the gas are burned from a bunsen burner, and the products of combustion passed through an apparatus consisting of a tube provided with six bulbs, inclosed in a larger tube through which a current of cold water flows. The liquid condensed in the bulb tube runs out through a narrow tube at the lower part of the apparatus, where it is collected in a flask. Sufficient hydrogen peroxide is added to the condensed liquid to oxidise the sulphurous acid, and the sulphuric acid is titrated by means of N/10 alkali, or estimated gravimetrically.

The apparatus may also be used for estimating sulphur in petroleum. L. DE K.

Microchemical Reaction for Nitric Acid. By J. L. C. SCHROEDER VAN DER KOLK (*Jahrb. f. Min.*, 1897, i, 219).—The following test, which is somewhat similar to that proposed by Brauns (this vol., ii, 343), has been used by the author for several years. The substance to be tested is placed with a drop of sulphuric acid in the hollow in a glass slide, and from the cover-glass hangs a drop of barium hydroxide solution; when nitric acid is driven off, typical crystals of barium nitrate appear in the drop on the cover-glass. As the substance tested does not come in contact with the barium solution, the presence of sulphates, phosphates, &c., does not affect the result. L. J. S.

Estimation of Hydrochloric Acid in the Gastric Juice. By HERMANN STRAUSS (*Chem. Centr.*, 1896, i, 1024—1025; from *D. Arch. Klin. Med.*, **56**, 87—120).—Dimethylamidoazobenzene, recommended by Töpfer for this purpose (Abstr., 1894, ii, 262), is ten times as sensitive as Congo red paper for the detection of free hydrochloric acid, but owing to the somewhat wide limits of the change from red

to yellow, the recognition of the neutral point is influenced by the differently developed sense of colour estimation in individuals. A 1 per cent. aqueous solution of Congo red is still more sensitive, and is best used by testing drops removed from the liquid under titration (Töpfer method), taking as the neutral point that at which a bluish-black colour is no longer observed in the contact zone of the two drops. Acid phosphate solutions, with both these indicators, produce changes which may be mistaken for those caused by highly dilute acids, as do also organic acids, especially lactic acid, when present in such proportions as occur in pathological human gastric juice. Töpfer's method of estimating the loosely combined hydrochloric acid with alizarin demands a highly developed power of recognising colour changes. In any case, a quantitative comparison of the amount of free hydrochloric acid with the total acidity affords a better means of judging whether the composition of the secretion exceeds the normal limits than a mere estimation of the total acidity with the qualitative detection of free hydrochloric acid. M. J. S.

Detection of Traces of Fluorine in Beer. By WILHELM WINDISCH (*Chem. Centr.*, 1896, ii, 60; from *Wchschr. Brauerei*, **13**, 449).—A litre of the beer (more or less according to the proportion of fluorine) is deprived of carbonic anhydride, filtered, heated to boiling, and mixed with 400 c.c. of hot lime-water. The clarified upper liquor is drawn off, and the precipitate collected on a linen filter, dried as far as possible by wrapping in the linen and pressing between filter paper, transferred to a platinum crucible, dried, and ignited. It is then pulverised in the crucible, moistened with 3 drops of water, and 1 c.c. of concentrated sulphuric acid added, the escaping gas being allowed to act on a large watch glass which has been coated with wax and etched through in the usual manner; the watch glass is cooled by ice-cold water. It is admitted that the whole of the fluorine is not contained in the precipitate, but that a further amount can be thrown down by a second treatment with lime water. M. J. S.

Detection of Soda or Borax in Milk. By P. SOLOMIN (*Chem. Centr.*, 1896, ii, 66; from *Hyg. Rundsch*, **6**, 445, *Hyg. Inst. Berlin*).—The author has tested a method suggested by Tscherbakoff, which consists in simply mixing the milk with an equal volume of 95 per cent. alcohol. Normal milk yields a coarse clot in, at most, half-a-minute. The clotting is delayed for 5 minutes by the presence of 0·06 per cent. of soda (Tscherbakoff says 0·02) and the clot is then a finely divided one. In milk 24 hours old, 0·1 per cent. of soda is required to hinder the coagulation, and 0·2 per cent. after 48 hours. Borax behaves similarly; 0·08—0·1 per cent. being the minimum that can be detected. M. J. S.

Rapid Method for the Estimation of Boric Acid in Milk. By GEORGES DENIGÈS (*J. Pharm.*, 1897, [vi], **6**, 49—54).—Although, according to Farrington (this vol., ii, 194), a solution of boric acid in milk shows a greater acidity than when the same amount of acid is dissolved in water, yet the author finds that, for solutions containing 1, 2, or 3 grams of boric acid per litre, the solutions in milk do not

exhibit so great an acidity as do corresponding solutions in water mixed with glycerol. The greater acidity in milk is due to milk-sugar. The method recommended is as follows. Twenty c.c. of milk is placed in each of two flasks, to one of which 2 or 3 drops of phenolphthalein and sufficient N/10 sodium hydroxide to cause a permanent pink tint are added; 10 c.c. of a mixture of equal volumes of ethylic alcohol (90°) and glycerol is then added, and subsequently sufficient N/10 sodium hydroxide to bring back the pink colour which had disappeared. If n = the number of c.c. of N/10 alkali required in the second case, then $n - 0{\cdot}15$ gives in grams the amount of boric acid in 1 litre of milk. The amount is correct to 1 or 2 decigrams. If the milk contains more than 3 grams of boric acid per litre, it is necessary to dilute before taking the 20 c.c. The method is only accurate when the amount of boric acid is below 3 grams per litre and the amount of milk-sugar is between 40 and 50 grams per litre. J. J. S.

Estimation of Sodium in Presence of Potassium. By FEODOR F. BEILSTEIN and O. VON BLAESE (*Zeit. anal. Chem.*, 1897, **36**, 513; from *Bull. Acad. Sci. de St. Pétersbourg*, **33**, 209).—To the solution of the chlorides or nitrates, a solution of potassium antimonate is added. The supernatant liquid is decanted after 24 hours and the precipitate washed, first with a 0·7 per cent. solution of potassium acetate, and then with 50 per cent. alcohol. After ignition, it is weighed as $NaSbO_3$. For each 100 c.c. of the decanted liquid (which must not contain potassium carbonate), 0·0233 gram must be added to correct for solubility. M. J. S.

Estimation of Alumina in Phosphates. By HENRI LASNE (*Zeit. angw. Chem.*, 1897, 276—278; reply by VON GRUEBER (*Zeit. angw. Chem.*, 1897, 278).—The first author (this vol., ii, 191) claims priority for the use of sodium hydroxide in the separation of aluminium phosphate from iron and the earthy phosphates (Abstr., 1892, ii, 233), and states that the few alterations proposed by von Grueber cannot be considered as improvements, but rather the reverse. In reply, the latter states that he was unacquainted with Lasne's investigation. L. DE K.

New and Rapid Method for the Qualitative Separation of Iron, Aluminium, Chromium, Manganese, Zinc, Nickel and Cobalt. By ALEXANDER R. CUSHMAN (*Amer. Chem. J.*, 1897, **19**, 606—607).—Precipitate with ammonium chloride, ammonia, and ammonium sulphide. Warm the well washed precipitate with moderately dilute hydrochloric acid in a porcelain dish; complete solution indicates the absence of nickel and cobalt, but if a black residue remains, this is dissolved by adding aqua regia. The excess of acid and chlorine is then expelled by evaporation, the solution made strongly alkaline with ammonia (after previously adding ammonium chloride in case the amount of hydrochloric acid used on the sulphides was small), bromine solution is added in excess, the whole allowed to remain a few minutes and filtered, giving precipitate (1) and filtrate (1).

The *precipitate* (1), removed from the filter, is treated with potassium hydroxide in excess and with bromine solution, and filtered, the *filtrate*

being (2). A portion of the *residue* is dissolved in hydrochloric acid and tested for iron with thiocyanate; another portion is tested for manganese by fusion with sodium carbonate and nitrate. A portion of the filtrate (2) is acidified with hydrochloric acid, treated with excess of ammonium carbonate, and boiled, to see if aluminium is present; another portion is tested for chromium with acetic acid and lead acetate.

To the original *filtrate* (1), a large excess of potassium hydroxide is added, and the whole filtered after a few minutes. The greenish-white *precipitate* (2) is nickel, and is confirmed by the blow-pipe test with a bead of microcosmic salt. The *filtrate* (3) from this is boiled, when cobalt is precipitated, and is confirmed by the borax bead, whilst the filtered solution (4) is tested for zinc by acidifying with acetic acid and saturating with hydrogen sulphide, the presence of the metal being confirmed by igniting the precipitate with cobalt nitrate on charcoal.

C. F. B.

Estimation of Carbon in Iron. By LEOPOLD SCHNEIDER (*Chem. Centr.*, 1896, i, 1026; from *Oesterr. Zeit. Berg-Hütt.*, **10**, 121).—The author has improved his process (Abstr., 1895, ii, 531) by substituting phosphor-copper for the copper powder. Phosphor-copper, containing 15 per cent. of phosphorus, is easily powdered, and burns in oxygen more readily than pure copper. It should be freed from iron by digesting for 24 hours with concentrated hydrochloric acid and washing with water, and a blank combustion with 10 grams should be made to prove the absence of carbon. In other respects, the process is not altered.

M. J. S.

[**Analysis of Ilvaite.**] By K. H. SCHNERR (*Jahrb. f. Min.*, 1897, i, 432 Ref.; from *Inaug.-Diss. München*, 1894). See this vol., ii, p. 507.

Estimation of Manganese in Presence of Phosphoric Acid. By GEORGES VIARD (*Bull. Soc. Chim.*, 1896, [iii], **15**, 973—975).—The method for the estimation of manganese proposed independently by Hannay, and by Beilstein and Jawein consists in adding potassium chlorate in successive small quantities to the manganese solution, strongly acidified with nitric acid and heated to boiling, the precipitated peroxide being collected, ignited, and weighed. The author calls attention to the fact that this method is inapplicable in presence of phosphoric acid, owing to the precipitation of trimanganic phosphate under the conditions of the experiment.

A. C. C.

Volumetric Estimation of Zinc. By K. DEMENTÉEFF (*Chem. Centr.*, 1896, ii, 207; from *Pharm. Zeit. Russ.*, **35**, 263).—The zinc compound, which must be free from heavy metals, is dissolved in soda, and in a portion of the solution the total bases are titrated by acid, using as indicator tropæolin, which gives a yellow colour with alkali, and orange-red with acid. In another portion, the soda alone is titrated with phenolphthalein, and the zinc is calculated from the difference between the two titrations.

M. J. S.

Quantitative Analysis by Electrolysis. By E. WAGNER (*Chem. Centr.*, 1896, ii, 58—59; from *Zeit. Elektrotech. und Elektrochem.*, **2**,

613—616).—*Copper.*—In a platinum basin of 100 square cm. effective surface, with an anode of perforated platinum foil 45 mm. in diameter, 1 gram of $CuSO_4$ can be electrolysed ; for this purpose, the copper solution is added to a solution of 4 grams of ammonium oxalate in 60 c.c. of water, the temperature is raised to 60°, and the solution electrolysed for 30 minutes with a current of 0·05 ampère ; 5 c.c. of cold saturated solution of oxalic acid is then added, the current increased to 0·5 ampère, and during the next 80 minutes 5 c.c. of oxalic acid is added four times. Deposition is complete in 2 hours. The copper is washed with water and alcohol as usual, and dried for 5 minutes at 100°. *Zinc.*—The solution containing 1·5—1·8 gram of $ZnSO_4$ in 40 c.c. of water is gradually added to one of 4 grams of ammonium oxalate in 60 c.c. The solution is heated to 55—60°, and electrolysed with 0·2 ampère ; 15 minutes later, 5 c.c. of 6 per cent. tartaric acid solution is added, taking care not to pour it on the anode, and during the next 2 hours this addition is 5 times repeated, whilst the current is augmented to 0·4—0·5 ampère, with an electromotive force of 3—3·2 volts. The deposition is complete in 2—2½ hours. The zinc is washed and dried like the copper, but at 70°. M. J. S.

Employment of Cupric Salts in the Analysis of Irons and Steels. By ADOLPHE CARNOT and GOUTAL (*Compt. rend.*, 1897, **125**, 75—80).—*Carbon.*—The ordinary operation of dissolving iron or steel in cupric chloride for the estimation of carbon can be greatly accelerated, without any risk of loss of carbon, by placing in the bottom of the flask used a perforated disc of platinum about 11 cm. in diameter, and employing, for each gram of metal taken, 50 c.c. of a 30 per cent. solution of cupric potassium chloride and 4 or 5 drops of hydrochloric acid. A current of carbonic anhydride is passed into the liquid, so that the upper part of the flask is continually filled with this gas. The copper solution is first placed in the flask, heated to boiling for a few minutes, cooled to 60°, and the iron or steel added, the whole being afterwards heated at 90—95°. Fine filings are dissolved in 20 minutes, and even lumps of 5 grams are dissolved in an hour and a half. The residue is treated in the usual way, and should be burnt in oxygen without being previously dried.

Sulphur.—When iron or steel is dissolved in very slightly acidified cupric potassium chloride solution under the conditions specified, all the sulphur remains in the insoluble residue, which is well washed and treated with a mixture of 5 c.c. of hydrochloric acid, 15 c.c. of water, and 1 c.c. of bromine for some time in the cold, then slowly heated, and finally boiled. The liquid is neutralised with ammonia, re-acidified with a small quantity of hydrochloric acid, and the sulphuric acid precipitated with barium chloride. The whole estimation can be completed in 3 hours.

Phosphorus.—If the cupric potassium chloride solution is quite neutral, all the phosphorus remains in the residue, which is treated with nitric acid and bromine, filtered, boiled with some chromic acid to oxidise hydrocarbons, neutralised with ammonia, reacidified with nitric acid, and precipitated with ammonium molybdate. The precipitate has its normal composition. Any arsenic present is dissolved by the copper solution.

Chromium.—With a neutral copper solution, the chromium remains in the residue, which can be heated with sodium peroxide, the chromic acid being estimated in an aqueous solution of the fused mass.

Tungsten and Titanium.—The residue left by the neutral copper solution is treated with hydrofluoric acid to remove silica, and then fused with a mixture of 4 parts of potassium nitrate and 1 part of potassium carbonate. The product is treated with water, and the tungsten estimated in the solution by means of mercurous nitrate (Defacqz, this vol., ii, 163). The residue containing the titanium is fused with potassium hydrogen sulphate, dissolved in water, and mixed with sulphurous acid to reduce the ferric sulphate; sodium acetate is then added, the liquid boiled, and the titanium oxide collected and weighed.

When there is doubt as to the nature of the precipitate, it is heated with a small quantity of potassium hydrogen sulphate and a few drops of sulphuric acid. After cooling, a crystal of quinol is added; titanium gives a carmine-red coloration (Lévy), whilst tungsten gives an amethyst-violet coloration (Defacqz).

To detect traces of tungstic acid, the residue left by the copper solution is washed, treated with hot concentrated ammonia, and the liquid evaporated to dryness. The residue is treated in the manner just described. C. H. B.

Electrolytic Analysis of Bronze and Brass. By A. Hollard (*Compt. rend.*, 1897, **124**, 1451—1453).—Five grams of the bronze or brass is dissolved in a mixture of 25 c.c. of nitric acid of 36° B. and 15 c.c. of concentrated sulphuric acid, and the liquid is diluted to 350 c.c. and heated nearly to its boiling point until any undissolved stannic oxide readily agglomerates and settles to the bottom of the vessel. The estimation of the copper is conducted in the manner previously described (this vol., ii, 161), and the residual liquid is evaporated nearly to dryness. The tin is precipitated as sulphide, washed, dissolved in ammonium sulphide, the solution evaporated to dryness, and the residue treated with potassium chlorate and excess of hydrochloric acid. The solution thus obtained is evaporated to dryness, dissolved in 30 c.c. of hydrochloric acid diluted with water, 30 grams of pure ammonium oxalate added, and the tin precipitated with a current of 0·7 ampère, the liquid being kept at a temperature of about 90°, and the electrodes being slightly roughened. The roughening is effected by depositing zinc on the electrodes, removing it by means of nitric acid, and afterwards immersing the electrodes in fused potassium hydrogen sulphate, the whole process being repeated if necessary.

The liquid from which the copper and tin have been precipitated is heated to expel hydrogen sulphide, evaporated almost to dryness, dissolved in water, neutralised with ammonia, mixed with 15 c.c. of a 10 per cent. ammonium citrate solution, 13·8 gram of ammonium acetate (or 9·4 c.c. of glacial acetic acid neutralised with ammonia), and 3 c.c. of glacial acetic acid; on submitting the solution to the action of a current of 0·6 ampère for about 12 hours, all the zinc is precipitated. Iron, if present, is partially precipitated with the zinc, but the amount is readily estimated by means of permanganate. Lead, if present, is precipitated as peroxide (*loc. cit.*). C. H. B.

Electrolytic Estimation of Lead. By O. von Giese (*Chem. Centr.*, 1896, i, 1209, 1284—1285; from *Zeit. Elektrotech. u. Elektrochem.* 2, 586—588. See Abstr., 1894, 161, 217, 480; 1895, ii, 418).—The author has revised the work of Kriechgauer on this subject. Whilst the deposition of lead as dioxide from a solution of the nitrate is favoured by the rise of temperature, this should not exceed 60°, since, at 70°, the deposition is incomplete in consequence of the decomposition of nitric acid. Between 50° and 60°, the time of deposition varies directly with the amount of lead present, and inversely with the area of the electrodes. At this temperature, a current of 0·5—1 ampère gives the best yield, and the deposits are dense, adhere well to the basin, and can be dried completely at 80—100°. Electrodes with a matt surface are recommended. Increase of potential shortens the time of deposition more than increase of current; about 0·95 volt. being the minimum. To prevent precipitation of lead on the cathode, 15 per cent. of nitric acid must be added to a 2·5 per cent. solution of lead nitrate, 17·5 per cent. of acid to a 3·75 per cent. solution of lead salt, and 20 per cent. of acid to a 5 per cent. solution. On a capsule with 180 square centimetres of surface, 5·5 grams of lead dioxide can be deposited. M. J. S.

New Reactions of Vanadic Acid, Molybdic Acid, and Thiocyanates. By W. Ellram (*Chem. Centr.*, 1896, ii, 211, 212; from *Sitzungsber Naturforsch. Ges. Univ. Dorpat*, 1895, 28).—A solution of potassium thiocyanate (1 : 12,000) treated with a vanadate and a trace of sulphuric acid, becomes yellow; with a little more acid, blue. Thiocyanates can thus be detected in saliva, serum, and milk (after removing albumin, &c., from the two latter by zinc sulphate). Similarly, vanadic acid, at a dilution of 1 : 5000, can be detected by thiocyanate. Molybdic acid similarly treated gives yellow, orange, and blood-red colorations. Even at a dilution of 1 : 1,000,000, a rose colour is perceptible. M. J. S.

Estimation of Gold and Silver in Auriferous Minerals. By P. Truchot (*J. Pharm.*, 1897, [vi], 5, 493—495; from *Ann. Chim. analyt.*).—The mineral is finely ground so as to pass through a No. 80 sieve, and 100—200 grams of the powder is then roasted in a muffle so as to destroy pyrites, arsenides, tellurides, &c., stirring from time to time. The roasted mineral is then transferred to a flask, covered with saturated bromine water, and digested for 36 hours, fresh bromine water being added if the liquid becomes colourless. The solution is now filtered, the residue well washed, and the filtrate and washings, after acidification with hydrochloric acid, are evaporated in a porcelain basin to about 200 c.c. If necessary, the solution is again filtered, and the gold is then precipitated by a solution of ferrous sulphate acidified with sulphuric acid. The residue obtained above, after treatment with bromine water, contains the silver in the form of silver bromide; this can be dissolved out by concentrated ammonium chloride, and then precipitated in the usual way as silver bromide. J. J. S.

Destruction of Organic Matter in Toxicology. By Antoine Villiers (*Compt. rend.*, 1897, 124, 1457—1458).—The matter is

mixed with hydrochloric acid diluted with 2 or 3 times its volume of water, or less in special cases, and a few drops of a solution of manganese and a small quantity of nitric acid are added; the flask is then carefully heated, fresh quantities of nitric acid being added from time to time. The gases evolved consist of almost pure carbonic anhydride and nitrogen, and decomposition proceeds regularly without any formation of obnoxious volatile products. All the softer organs are very rapidly destroyed, but muscular fibre requires about an hour. The only substance that remains unoxidised is fat, which seems to be partially converted into substitution products. C. H. B.

Estimation of Dry Matter in Peat. By HEINRICH C. TRYLLER (*Landw. Versuchs-Stat.*, 1897, **49**, 145—161).—A number of estimations of dry matter in peat are given. The figures show that, for most purposes, sufficiently concordant results are obtained by heating at 105°, and allowing it to cool over sulphuric acid. The very divergent results obtained by Puchner (Abstr., 1895, ii, 544) could not have been due either to oxidation or to absorption of acid vapours from ordinary sulphuric acid as suggested.

A modified form of L. Meyer's air-bath was used in the experiments, and is described, with sketch. N. H. J. M.

Estimation of Paraffin. By HERMANN EISENLOHR (*Zeit. angw. Chem.*, 1897, 300—302; 332—336).—The author has proved, by a large number of experiments, that the methods now in use for the estimation of paraffin, are only fit for the assay of hard paraffins; they utterly fail when testing soft paraffins. The following process is recommended when dealing with a brown-coal product containing not more than 14 per cent. of oily matter, and melting between 31·5° and 60°. 0·5 gram of the sample is dissolved in 100 c.c. of absolute alcohol; 25 c.c. of water is slowly added, stirring, meanwhile, with a thermometer, and the vessel is placed in a freezing mixture made of equal parts of ice and salt, so as to cool the mixture to −18 or −20°. After a short time, the paraffin has quantitatively separated, and is then collected on a filter previously dried at 35°; the funnel is, of course, placed in an apparatus, the temperature of which does not exceed −18°. The precipitate is washed with alcohol of the same strength, until the filtrate no longer becomes turbid on adding water; the filter and contents are then dried to constant weight in a vacuum at 35—40°; this generally takes from 6 to 8 hours. L. DE K.

Detection of "Rosin Oil" in Turpentine. By A. AIGNAN (*Compt. rend.*, 1897, **124**, 1367—1368).—The method previously described (Abstr., 1890, 422) is not applicable when the proportion of "rosin oil" is below 2 per cent. When pure turpentine is distilled, the rotatory power of the successive fractions diminishes, and the same phenomenon is observed with turpentine mixed with rosin oil, but in the latter case the residue left in the retort has a much lower rotatory power than the corresponding residue from the pure substance. For example, the residue of 70 c.c. from 250 c.c. of pure turpentine, had a rotatory power of −51·5°; the corresponding residue from turpentine adulterated with 3 per cent. of rosin oil, had a rotatory

power of only $-36{\cdot}21°$, whilst with 5 per cent. of rosin oil, the rotatory power was only $-28{\cdot}6°$.

When n per cent. of rosin oil is introduced into turpentine, the rotatory power of a similar residue, in a column 200 mm. long, is reduced by *at least* $n \times 5° 30'$. Further, by distilling at 100° under a pressure of 60 mm., it is possible to obtain a *dextrogyrate* residue from a turpentine containing only 0·5 per cent. of rosin oil.

C. H. B.

Estimation of Chloroform in Viscera. By BERNHARD FISCHER (*Zeit. anal. Chem.*, 1897, **36**, 549; from *Jahresb. chem. Untersuchungsamts der Staadt Breslau*, April, 1894, to March, 1895).—After the viscera have been distilled with water until all the chloroform has passed over, the distillate is mixed with potassium carbonate, warmed to 60°, and washed air aspirated, first through the liquid, then through a combustion tube heated to bright redness, and finally through a solution of silver nitrate. In chloroform poisoning, the chloroform is found chiefly in the blood and brain. In all cases, its presence must be confirmed by the isonitrile reaction.

M. J. S.

Examination of Chloroform. By AUGUSTE BÉHAL and MAURICE FRANÇOIS (*J. Pharm.*, 1897, [vi], **5**, 417—424).—It is well known that pure chloroform cannot be kept for any length of time, as it decomposes in contact with air and in presence of sunlight, evolving carbonyl chloride; the admixture of a little alcohol, however, prevents the decomposition taking place. The author has examined a number of specimens of chloroform, and finds that the only impurities are water and alcohol. The water causes the chloroform to partially solidify when cooled to between $-20°$ and $-40°$. An accurate method of estimating the amount of alcohol present is described; for this purpose, the chloroform is shaken with strong sulphuric acid, and the alcohol is thus removed in the form of ethyl hydrogen sulphate; when the acid extract is boiled with water, this is decomposed, and the alcohol can be distilled off and estimated by oxidation to acetic acid. J. J. S.

Estimation of Maltose in Worts. By LUDWIG BRAUN (*Chem. Centr.*, 1896, ii, 67—68; from *Zeit. ges. Brauw.*, **19**, 241, 254).—The conventional method laid down in 1890 by the Vienna Conference is in many respects incomplete. Experiments show that the estimation should take place as soon as possible after the clarifying of the wort. The choice of vessels is important. The conference prescribed capsules of 13 cm. diameter; the use of capsules 9 cm. diameter, which give the same results, is general, but they should always be covered when in use. Shallower basins give lower results. Glass vessels do not give the same results as those of porcelain, either from their different heat conductivity, or from the difference in the surface exposed. In accordance with the Vienna instructions, the Fehling's solution should first be heated to boiling, then the wort added, and the boiling continued for 4 minutes. Filtration should take place immediately, without the addition of the 50 c.c. of cold water prescribed by Kusserow, which leads to lower numbers. Kjeldahl's method (Abstr., 1896, ii, 580) gives widely different results, mainly in consequence of the longer

heating, and the author gives the preference to the Vienna method, if the above precautions are observed. M. J. S.

Estimation of Milk-Sugar in Milk. By HENRY DROOP RICHMOND and L. KIDGELL BOSELEY (*Analyst*, **22**, 1897, 98—100).—The authors have recalculated the figures on the strength of which Wiley and Ewell (Abstr., 1896, ii, 628) recommended their process for the estimation of lactose in milk, and have found them to be erroneous, so that the experimental error is about twice as great as those chemists supposed.

A slight modification of Vieth's process is described; this consists in clarifying the sample with mercuric nitrate and then making a correction for the volume of the deposit. To 100 c.c. of milk, 3 c.c. of acid mercuric nitrate is added to compensate for the volume of the proteids; as much water as corresponds with the fat multiplied by 1·11; then, again, as much water as corresponds with one-tenth of the degrees of specific gravity, and also a sufficient volume of water to reduce scale readings to percentages of milk-sugar. So if a milk contain 3·7 per cent. of fat and has a specific gravity of 1·0325, then $3 + 4·1 + 3·25 + 10$ (if a Mitscherlich half-shadow polariscope is used) $= 20·35$ c.c. must be added to 100 c.c. of the sample. In this way, calculation is dispensed with. L. DE K.

Estimation of Starch in Cereals. By LÉON LINDET (*Bull. Soc. Chim.*, 1896, [iii], **15**, 1163—1164).—The grain, about 10 grams in weight, after being bruised, is transferred to a conical flask, covered with a solution containing 1·5 per cent. of hydrogen chloride and 2 per cent. of pepsin, and the whole kept for 12—24 hours at 40—50°. The pepsin serves to destroy the gluten, which forms a network round the starch granules, and the hydrochloric acid prevents the action of the diastase on the starch. The flask is occasionally shaken, and the contents are then poured on to a piece of silk such as is used for dressing flour (No. 80—100), the silk is folded and then kneaded several times with fresh quantities of water until no more starch escapes from the silk. The combined amylaceous liquids are mixed with a little formaldehyde or mercuric chloride and then poured on to a tared filter. The filtration is tedious, and may be hastened by the addition of a weighed quantity of washed and calcined pumice. J. J. S.

Estimation of Starch in Sausage Meat. By JOSEPH MAYRHOFER (*Chem. Centr.*, 1896, ii, 70; from *Forsch.-Ber. Lebens und ihre Bez. z. Hyg.*, **3**, 141).—A quantitative estimation is necessitated by the fact that, in some German districts, the addition of 2—3 per cent. of farina is officially permitted. The author makes use of the fact established by Dragendorf, that starch is insoluble in alcoholic potash, whilst sugar, fat, albumin, &c., are dissolved. For this purpose, 60 grams of the sample is digested on the water bath with an 8 per cent. alcoholic potash solution. In the absence of starch, everything will dissolve except cellulose. The solution is diluted with hot alcohol, and the insoluble matter collected on a filter and washed with alcohol until free from alkali. It is then dissolved in aqueous potash, and the solution acidified with acetic acid. The starch is precipitated by the addition of alcohol, collected, washed, dried, and weighed. M. J. S.

Distinctive Reaction for α- and β-Naphthol. By EUGÈNE LEGER (*J. Pharm.*, 1897, [vi], 5, 527—529).—A solution of sodium hypobromite is made by diluting 30 c.c. of sodium hydroxide solution (36° B.) with 100 c.c. of water, then adding 5 c.c. of bromine and shaking vigorously. Two drops of the above solution are added to 10 c.c. of a saturated aqueous solution of α- or β-naphthol, obtained by triturating the solid naphthol for some few minutes with water. In the case of the α-compound a dirty violet coloration, and even a precipitate, is formed; the reaction is very sensitive, and occurs when the naphthol solution is diluted with 9 volumes of water. In the case of β-naphthol, a yellow coloration is developed; this gradually becomes greenish and then again yellow. If the solution of the β-compound is diluted with its own volume of water, and treated in exactly the same way as described above, a yellow coloration is formed, but it disappears on shaking. By means of this test, 1 part of α-naphthol can readily be detected in 100 parts of β-naphthol. In making the tests, freshly prepared solutions must be used. J. J. S.

Schiff's Reaction with "Acid Magenta." By LEON LEFÈVRE (*Bull. Soc. Chim.*, 1896, [iii], 15, 1169—1171. Compare Cazeneuve, Abstr., 1896, ii, 630).—The author points out that the only difference in Schiff's reaction when using "acid magenta" instead of rosaniline hydrochloride itself is that the violet colour takes a slightly longer time to develop. J. J. S.

Distillation of Formaldehyde from Aqueous Solutions. By NORMAN LEONARD, HARRY M. SMITH, and HENRY DROOP RICHMOND (*Analyst*, 1897, 22, 92).—When distilling a solution of formaldehyde, the amount of the latter found in any fraction is expressed by the formula, $100 - y = \frac{(100 - x)^{1\cdot65}}{100^{0\cdot65}}$, in which y represents the percentage of formaldehyde in the distillate and x the volume of the fraction expressed as percentage.

Several analyses are given to prove the correctness of the formula, and also a table of the rates of distillation of formaldehyde, and of formic, acetic, propionic, and butyric acids. L. DE K.

Estimation of Aldehyde in Ether. By MAURICE FRANÇOIS (*J. Pharm.*, 1897, [vi], 5, 521—525).—The author makes use of the following solution. Water recently saturated with sulphurous anhydride 220 c.c., magenta solution (1 in 1000) 30 c.c., and sulphuric acid (66°) 3 c.c. A mixture of 5 c.c. of pure ether, 5 c.c. of 95 per cent. pure alcohol, and 4 c.c. of the above solution remains colourless for 15 minutes; if the ether contains more than 1/10000 part of aldehyde, the mixture assumes a reddish-violet colour, the intensity of the colour depending on the amount of aldehyde present. The amount of aldehyde in the ether is readily determined by comparing the intensity of the colour produced by it with that produced by 5 c.c. of alcohol containing 1/1000 or 1/10000 part of pure aldehyde, mixed with an equal volume of pure ether. J. J. S.

Estimation of Benzaldehyde in "Kirschwasser." By L. CUNIASSE and SIG. DE RACZKOWSKI (*Zeit. anal. Chem.*, 1897, 36, 403; from *Mon.*

sci., [iv], **8**, II, 915).—Two hundred c.c. of Kirschwasser is distilled as completely as possible, and the distillate made up to the original volume; 3—4 c.c. of a freshly-prepared solution containing 2 grams of phenylhydrazine hydrochloride and 3 grams of crystallised sodium acetate in 20 c.c. is added, and then water to make it up to 400 c.c. The precipitated benzylidenephenylhydrazine is collected, washed with very dilute alcohol, and dissolved in 10 c.c. of absolute alcohol; the alcoholic solution is then evaporated in a vacuum, and the residue weighed. One part corresponds with 0·54 part of benzaldehyde. M. J. S.

Recognition of Certain Organic Acids in Plants. By ARMAND BERG and C. GERBER (*Bull. Soc. Chim.*, 1897, [iii], **15**, 1050—1055. Compare Abstr., 1895, ii, 297).—Citric acid may be detected in presence of oxalic, tartaric, and malic acids in the following manner. The dry substance is heated with 5—6 parts of sulphuric acid (66° B.) during $1\frac{1}{2}$ hour at 50—60°, cautiously diluted with water (5 vols.), and extracted with ether, which is then removed, and evaporated in two separate portions. One part of the residue is dissolved in water and treated with a dilute solution of ferric chloride, which develops a reddish-violet coloration; the remainder is treated with a dilute, freshly-prepared solution of sodium nitroprusside, and subsequently with a drop of concentrated soda, when an intense red coloration is produced. These colour changes depend on the conversion of citric into acetonedicarboxylic acid under the influence of sulphuric acid.

Although the test already described (*loc. cit.*) is applicable to citric, tartaric, and malic acids, the last-named may be distinguished in presence of the other two on account of the solubility of the ammonium salt in alcohol; if ammonia is passed into an alcoholic solution of the acids, the residue obtained on evaporating the filtrate gives the indication in question only when malic acid is present.

The authors describe their scheme for recognising organic acids in plants, based on these additions to existing methods. M. O. F.

Simple Method of Estimating Fat in Centrifugalised Cream. By MATS. WEIBULL (*Bied. Centr.*, 1897, **26**, 491—492; from *Kongl. landtbr.-akad. handl. tidskr.*, 1896, 370—379).—The proposed method depends on the relation between the amounts of fat (f) and dry matter (d) contained in cream. This relation is expressed by the equation: $d = f + \frac{100-f}{100}/$ constant. The constant being 8·7, $f = 1{\cdot}1\,d - 9{\cdot}5$.

The dry matter of the cream is determined by mixing about 6 grams with finely powdered pumice (20 c.c.) and heating for $2\frac{1}{2}$ hours at 100°.

A number of determinations were made by this method, most of which (71 per cent.) showed an error of less than 0·5 per cent. Only in one case did the error amount to 1 per cent. N. H. J. M.

Cryoscopy applied to the Analysis of Milk. By E. CARLINFANTI (*Gazzetta*, 1897, **27**, i, 460—466).—Using the Beckmann cryoscopic apparatus, the author shows that the freezing point of milk is $-0{\cdot}55°$ to $-0{\cdot}59°$; as the milk becomes changed by keeping,

its freezing point falls, but a milk freezing at $-0{\cdot}59°$ cannot be described as bad. The experiments show that the freezing point is quite independent of the proportion of fats or proteids present, but is determined by the quantity of material actually in solution; the addition of a 9 per cent. lactose solution, freezing at $-0{\cdot}55°$ to $-0{\cdot}59°$, to the milk does not alter its freezing point. The freezing point is, however, raised by $0{\cdot}05°$ to $0{\cdot}065°$ for each 10 per cent. of water added.

The cryoscopic method can thus be used to detect the adulteration of milk. W. J. P.

Detection of Mixtures of Diluted, Condensed, or Sterilised Milk with Fresh Milk. By HENRY DROOP RICHMOND and L. KIDGELL BOSELEY (*Analyst*, 1897, **22**, 95—97).—The authors base their process on the fact that sterilised, or diluted, unsweetened, condensed milk throws up its cream slowly and imperfectly; the albumin has also undergone alteration and the rotatory power is affected.

One hundred c.c. of the sample is put into a creamometer for 6 hours at 15·5° and the percentage of cream is read off. At least 2·5 per cent. of cream should rise for every 1 per cent. of fat in the milk; so if the amount of the cream falls below 2 per cent. for each 1 per cent. of fat, sterilised (or unsweetened condensed) milk is likely to be present.

The albumin is then estimated by the Sebelein and Duclaux method. If less than 0·35 per cent. is found, sterilised milk may be considered to be present. Further evidence may be obtained from the result of a polarimetric observation; if much sterilised milk is present, the amount of lactose thus found will be less than that obtained by a gravimetric experiment.

A fairly good quantitative approximation may be obtained by using the formula:

$$\text{Percentage of sterilised milk} = 100\frac{0{\cdot}4 - \text{per cent. soluble albumin}}{0{\cdot}4}$$

or from the cream rising test: $\text{Percentage of sterilised milk} = \dfrac{2{\cdot}5 - C/F/.}{2{\cdot}2}$

L. DE K.

Characterisation of Margarine by Admixture of Starch. By FRANZ SOXHLET (*Bied.-Centr.*, 1897, **26**, 489—490; from *Milchzeit.*, 1897, No. 2, 17).—As regards the addition of starch to margarine instead of phenolphthalein, as recommended by the author, it is pointed out that whilst the limit of the iodine reaction is only reached when 1 gram is diluted with 50,000 parts of water, the reaction is much less delicate in presence of milk, when 1 gram of starch in 10,000 parts of milk can just be detected. To detect 20 per cent. of margarine in butter, the milk employed in the preparation of margarine would have to contain 7·5 grams of starch per litre, an amount which would be injurious to the keeping quality of the margarine. An objection raised against phenolphthalein is that it can be washed out. The same holds for starch, which can, moreover, be destroyed by the addition of malt extract. Raw starch would not have this disadvantage, but at least

1 per cent. would have to be added to margarine to show the iodine reaction.

The detection by means of raw starch is much more sensitive if the margarine is melted and the liquid underneath the fat treated with iodine; a reaction is then obtained with 2 grams of starch in 100 kilograms of margarine, or with butter containing 20 per cent. of margarine with 0·01 per cent. of starch. Raw starch, however, could not be employed with the margarine generally used in South Germany, as it does not dissolve in fat.

The detection of phenolphthalein is more simple than that of starch when the butter has to be first melted; and, finally, it is pointed out that genuine butter may easily come into contact with flour, and thus become liable to suspicion. N. H. J. M.

Assay of Linseed Oil. By WALTHER LIPPERT (*Zeit. angw. Chem.*, 1897, 306—307).—The paper is a criticism of Amsel's pamphlet on linseed oil and linseed oil varnish.

The author attaches great importance to the heating test. A good oil must remain clear even when heated to 300° and not give any flocculent deposit. The drying test depends, not only on the quality of the oil, but a good deal on the nature of the drier. A solution of manganous resinate in oil of turpentine containing a definite proportion of rosin and manganese might perhaps be found serviceable.

L. DE K.

Detection of Arachis Meal and Arachis Cake in Chocolate. By BILTERYST (*J. Pharm.*, 1897, [vi], **6**, 29—30).—The examination may be made either microscopically or chemically. In the latter case, the fatty matter is extracted with carbon tetrachloride, and its refractive index determined in a Jean and Amagat's oleorefractometer. The index for cocoa fat is $-19°$, whilst for arachis it is $+3°$. A mixture containing 5 per cent. of arachis has an index $-18°$, and one containing 50 per cent. an index of $-7°$. This test can be supplemented by the determination of the proteids present, since chocolate contains 9, cocoa 18, arachis meal 20, and arachis cake about 45—47 per cent. of proteids. J. J. S.

Detection of Japanese Wax and Tallow in Beeswax. By L. S. LUGOWSKY (*J. Pharm.*, 1897, [vi], **5**, 295—296; from *Pharm. Zeit. Russ.*, 1896, **35**, 839).—The method commonly used is as follows: 50—60 grams of the suspected wax is distilled from a small retort, the distillate is washed with water and filtered, and the filtrate treated with a solution of lead acetate; the formation of a precipitate proves the presence of some fatty material in the original wax. The author, however, recommends the following process. The suspected sample is heated with a solution of borax saturated in the cold; if tallow is present, a white turbidity is produced, and if Japanese wax is present, a milky liquid. When cold, a layer of fat will be found under the layer of wax. The tallow and Japanese wax may be further identified by liberating the glycerol from them, and oxidising it to formic acid by means of potassium permanganate. J. J. S.

Iodine Number of Cacao Butter. By D. HOLDE (*Zeit. anal. Chem.*, 1897, **36**, 381).—The maximum limit 51, given by De Negri and Fabris

in their monograph "Gli Olii," as also in the *Zeit. anal. Chem.*, 1894, **33**, 547 (Abstr., 1895, ii, 247), was quoted from the 1886 edition of Benedikt's *Analyse der Fette und Wachsarten*, p. 253, where it is erroneously given as Hübl's result. The number actually published by Hübl was 34. (See also Abstr., 1896, ii, 680). M. J. S.

Detection of Tannin. By BAEMES (*Zeit. anal. Chem.*, 1897, **36**, 518; from *Drug. Circ.*, **40**, 12, 308).—A solution is used containing 1 gram of sodium tungstate and 2 grams of sodium acetate in 10 c.c. In acid or alkaline solutions of tannin, this produces a straw-yellow precipitate insoluble in water. M. J. S.

Estimation of Tannin. By EUGEN AWENG (*J. Pharm.*, 1897, [vi], **5**, 294—295; from *Apoth. Zeit.*, 1896, 831).—Formaldehyde reacts with tannins, yielding insoluble condensation products known as tannoforms. The author has made experiments in order to determine whether this reaction could not be made use of in the estimation of tannin. The results in all cases come far too low, so that the method is altogether inapplicable. J. J. S.

Adulteration of Sumach. By MATTEO SPICA (*Gazzetta*, 1897, **27**, i, 349—358).—Silician sumach, especially when exported in the form of powder, is often largely adulterated with the leaves of a tamarisk (*Tamarix africana*), or of mastic (*Pistachia lentiscus*); the author gives various methods for detecting the fraud.

One method consists in determining the nitrogen by Kjeldahl's method; sumach leaves contain 0·9127 (0·87—0·98) per cent. of nitrogen, those of *T. africana* 1·7690 (1·48—1·99) per cent., and those of *P. lentiscus* 1·6345 (1·47—2·01) per cent.

The composition of the ash derived from the leaves of the various plants also affords a criterion of the purity of samples of sumach, and is given in the appended table.

Ash.	Sumach. 6·60	*T. africana.* 12·40	*P. lentiscus.* 5·40
	Composition of Ash.		
Insoluble and SiO_2	24·05	37·10	6·20
CaO	29·95	8·53	25·30
SO_3	4·67	20·139	5·218
MgO	6·25	9·368	5·760
Fe_2O_3, Al_2O_3	7·15	7·400	7·410
CO_2	12·60	1·130	13·750
P_2O_5	3·344	1·1134	4·021
Cl_2	3·101	4·4050	5·321
K_2O	6·305	7·950	14·604
Na_2O	2·004	2·630	12·176
Total	99·424	99·7654	99·760

Another method of detecting adulteration is afforded by applying Löwenthal's method for estimating tannin. The tannin is precipitated from the sumach extract as "copper tannate" by a cuprammonium solution; if the sumach is pure, this precipitate is completely soluble in dilute sulphuric acid, if adulterated with *T. africana*, a brick-red precipitate is left undissolved, and if sophisticated with *P. lentiscus*, a whitish precipitate remains undissolved by the dilute acid.

A colorimetric method of ascertaining the purity of sumach is also given, depending on the comparison of the colour of the extract with that of a standard solution containing 0·150 gram of safranine in a litre of water. Five grams of the sumach is boiled with 500 c.c., of water for half an hour, the liquid cooled, made up to 500 c.c. and filtered; to 25 c.c. of the filtrate, in a beaker, is added 5 c.c. of basic lead acetate solution (having the sp. gr. 1·184 at 15° and containing about 250 grams of basic lead acetate per litre) and 15 c.c. of caustic potash solution (having the sp. gr. 1·155 at 15° and containing 180 grams of potash per litre). The solution is then evaporated to 15 c.c., when, if it remains reddish-brown and practically clear, the sumach is pure; if the solution is yellow and contains any considerable amount of precipitate, foreign matter is present. The 15 c.c. of solution is now diluted to 250 c.c. and filtered; when examined in the Duboscq colorimeter, it should be of the same tint as the standard safranine solution.

Further, on warming sumach extract with much potash and a few drops of molybdate solution, a chocolate brown precipitate is obtained, which, if *T. africana* is present, is greenish by reflected light, and has a yellowish-brown reflex if sumach or mastic alone be present.

W. J. P.

Estimation of Aloin in Aloes. By G. L. SCHAEFER (*J. Pharm.*, 1897, [vi], **5**, 296; from *Pharm. Zeit.*, 1897, **42**, 95).—Fifty grams of aloes is dissolved in 300 c.c. of warm water to which a few drops of hydrochloric acid have been added; when cold, the solution is separated from the resin, 50 c.c. of ammonia (20 per cent.) and a solution of 15 grams of calcium chloride in 30 c.c. of water are added, and the whole rapidly shaken. At the end of 15 minutes, the precipitate is well pressed, or separated by means of a centrifugal machine. The precipitate is triturated in a mortar with hydrochloric acid, and the free aloin and calcium chloride dissolved in as little water as possible; the solution is filtered if necessary, and the residue washed with boiling water: the aloin separates from its aqueous solution on cooling. The best yields are obtained when ice is employed. J. J. S.

Estimation of Theobromine in Cocoa and in Chocolate. By L. MAUPY (*J. Pharm.*, 1897, [vi], **5**, 329—332).—Five grams of finely powdered cocoa are first extracted with light petroleum (60 grams) by boiling, and leaving the two in contact for a day; the dry residue is then triturated with 2 grams of distilled water, and the moist substance heated for an hour with 20 grams of 15 per cent. solution of phenol in chloroform; when cold, the mixture is filtered, and the residue twice boiled with 15 grams of chloroform. The chloroform is distilled from the united chloroform extracts, and the residue is heated for at least half an hour at 100°; when cold, 40 grams of ether (65° B.) are added,

and the mixture, after being well stirred, is put on one side for 6 hours; by this means, the theobromine is precipitated, whilst caffeine, colouring matters, and the last traces of fat go into solution. The mixture is then poured on to a weighed filter paper and washed with several c.c. of ether. In the case of chocolate, the residue, after extraction with light petroleum, is triturated with 4 c.c. of alcohol (70°) instead of with water.

J. J. S.

New Method for the Estimation of Casein in Milk. By GEORGES DENIGÈS (*Bull. Soc. Chim.*, 1896, [iii], **15**, 1116—1126).—The milk (25 c.c.) is placed in a 200 c.c. flask, 20 c.c. of a N/10 solution of mercuric potassium iodide and 2 c.c. of glacial acetic acid are added, and the whole is made up to 200 c.c. The mixture is then passed through a folded filter, the first few drops being rejected, and 12—15 c.c. of ammonia and 10 c.c. of potassium cyanide solution (equivalent to N/10 silver nitrate) are added to 100 c.c. of the filtrate; finally, decinormal silver nitrate is run in until a permanent precipitate is just formed. If q = the number of 1/10 c.c. silver nitrate used, then the number of grams of casein per litre in the original milk can be found from the following table.

$q - 48$.	Casein in grams per litre.	$q - 48$.	Casein in grams per litre.	$q - 48$.	Casein in grams per litre.	$q - 48$.	Casein in grams per litre.
0	0	12	10	24	22·25	36	39
1	1	13	11	25	23·5	37	40·5
2	1·75	14	12	26	24·75	38	42·75
3	2·50	15	13	27	26	39	45
4	3	16	14	28	27	40	47
5	3·75	17	15	29	28	41	49
6	4·5	18	16	30	29·25	42	51·5
7	5·5	19	17	31	30·75	43	54
8	6·5	20	18	32	32	44	57·2
9	7·15	21	19	33	33·5	45	60
10	8	22	20	34	35	46	62·5
11	9	23	21	35	37		

J. J. S.

Detection of Santonin in Urine. By L. DACLIN (*J. Pharm.*, 1897, [vi], **5**, 534).—The urine (30—40 c.c.) is treated first with lead acetate, and finally with crystallised sodium sulphate; after filtration, the limpid urine is gently evaporated in two porcelain dishes. After evaporation, 1 or 2 drops of sulphuric acid are added to the one dish, and the mixture gently warmed; the immediate appearance of a violet coloration indicates the presence of santonin. The residue in the second dish is treated with a few drops of alcoholic potash, when, if santonin is present a rose coloration is produced. The urine may also be extracted with chloroform, the chloroform evaporated, and the residue tested as above. Rhubarb gives neither of the above tests.

J. J. S.

General and Physical Chemistry.

Series Spectra of Oxygen, Sulphur, and Selenium. By CARL RUNGE and FRIEDR. PASCHEN (*Ann. Phys. Chem.*, 1897, [ii], **61**, 641—686).—The authors have examined the compound line spectrum of oxygen, and give tables of the wave-lengths of the lines observed. In addition to the six triplets observed by Piazzi-Smyth, they find seven other triplets of similar character, these forming, with the other six, two distinct series. The differences between the rates of vibration of the three components of each triplet are, so far as this can be determined, the same. The thirteen triplets are distributed regularly over the spectrum, and the two series which they form are similar to those already observed with magnesium, calcium, strontium, zinc, cadmium, and mercury. There are, in addition to the triplet series, two other series of lines in the oxygen spectrum. These lines probably represent pairs, as the double character was distinctly observed in the case of four of the brightest.

Sulphur has a compound spectrum analogous to that of oxygen. Two series of triplets were observed, the first containing six and the second four. The differences in the rates of vibration of the three components are again about the same, and these differences are nearly five times greater than those obtained in the case of oxygen.

Selenium also has a compound spectrum, in which series of triplets appear; the appearances here are similar to those observed with oxygen and sulphur. H. C.

Spectrum of Carbon. By ARNAUD DE GRAMONT (*Compt. rend.*, 1897, **125**, 172—175 and 238—240).—When a condensed spark is allowed to play on fused alkali carbonates, the spectrum of the metal only is observed so long as the salt is in the flame, but if the flame is removed, the carbon lines appear, and their intensity increases with the difference of potential between the two sparking poles. A condensed spark on gas-carbon, purified by treatment with acids, shows the lines of many impurities, but Siberian graphite showed only a mixed band and line spectrum of carbon. The intensity of the bands increases in hydrogen, especially if the current of gas be rapid. On the other hand, the fused carbonates show only the carbon lines, and never the bands described by Swan. The method of experiment finally adopted by the author was to allow the condensed spark to impinge on the salt kept in fusion by passing an electric current through the platinum wire that supports the bead of salt, the whole being enclosed in a glass flask, through which hydrogen or any other gas can be passed.

The lines observed were 6578·5, 5662·2, 5648·6, 5641·0, 5379·9, 5151·6, 5144·6, 5132·9, 4267·0. In the case of the red doublet C_α, only the more refrangible component, at 6598·5, was observed, but the other line at 6584·0 was never observed even under widely varying conditions. The line 5695·1, described by Angström and Thalen, but

not photographed by Eder and Valenta, was seen rarely and irregularly, and seemed to be independent of the other lines. The author suggests that it may be an air-line. It was never observed with graphite in presence of hydrogen. The group 5662·2, 5648·6, and 5641·0 is readily, if faintly, visible, although it was not photographed by Eder and Valenta; on the other hand, the author was unable to observe the line 4556·3 of Eder and Valenta. The line C_β4267·0 is the strongest and most characteristic, and is the only line that has any value for analytical purposes; with a highly condensed spark, it broadens and becomes nebulous at the edges. The successive differences between the reciprocals of the wave-lengths show that the groups I and II are almost symmetrically arranged on either side of the intermediate line 5379·7.

Some of the cyanides, thiocyanates, and thiocarbonates show the same carbon spectrum as the carbonates. C. H. B.

Some Emission Spectra of Cadmium, Zinc, and the Haloid Compounds of Mercury and some other Metals. By A. C. JONES (*Ann. Phys. Chem.*, 1897, [ii], **62**, 30—53).—The emission spectra of cadmium and zinc, when the discharge is not a powerful one, consist of a number of bands built up of lines which decrease in intensity from the red to the violet end of the spectrum; these bands disappear when the discharge is a powerful one. The haloid compounds of mercury give a band spectrum, both in the visible and ultra-violet portions of the spectrum; in many cases, these bands consist of pairs of lines, but no numerical relationships could be established between them. Measurements of the wave-lengths are given. H. C.

New Lines in the Spark Spectrum of Aluminium. By GUSTAV A. HEMSALECH (*Phil. Mag.*, 1897, [v], **44**, 289—291).—During the examination of the aluminium spectrum obtained by means of a coil giving a 10-inch spark, a number of lines were observed which were previously unrecorded. The wave-lengths were determined by a grating and 2 prisms, the means of the three values being, (1) 6828·2; (2) 6842·6; (3) 6928·2; (4) 7042·5; (5) 7057·9. Of these lines, (4) and (5) are the brightest, and (5) is probably double. L. M. J.

Spectroscopic Investigation of the Blood. By LOUIS LEWIN (*Arch. Pharm.*, **235**, 245—255).—In these investigations, a Browning's pocket spectroscope was employed, a small glass bottle of about 2 c.c. capacity and having parallel sides being used to contain the specimen. The results of the experiments are shown in the form of a table giving the various absorption bands produced by oxyhæmoglobin, carboxyhæmoglobin, thiohæmoglobin, &c. J. F. T.

Crystalline Form of Optically Active Substances. By HERMANN TRAUBE (*Ber.*, 1897, **30**, 288. Compare this vol., ii, 2).—The author replies to Walden (*Ber.*, 1897, **30**, 98) and states that in all cases which have been completely examined, Pasteur's principle—that all optically active substances crystallise in non-superposably hemihedral forms—is found to hold. W. J. P.

Connection between Volume Change and Specific Rotation of Active Solutions. By RICHARD PŘIBRAM and CARL GLÜCKSMANN

(*Monatsh.*, 1897, **18**, 303—327).—The curve representing the relation between the percentage composition and the specific rotation of nicotine solutions may be regarded as built up of three different portions. The points of intersection would then lie at about 6 per cent. and 69 per cent. The addition of water to nicotine at first produces a very rapid fall in the rotation, but when the concentration of the nicotine reaches 69 per cent., the fall becomes less rapid, and from 6 per cent. onwards there is a rise in the rotation with increasing dilution. A solution containing about 69 per cent. of nicotine is the one that possesses the maximum density, and this point also coincides with the maximum volume contraction. The solution approximates to the composition $C_{10}H_{24}N_2 + 4H_2O$, and the authors are inclined to refer the peculiarities noticed in nicotine solutions to the existence of hydrates.

H. C.

Production of Electricity by Chemical Means. By ERNST ANDREAS (*Zeit. Elektrochem.*, 1896, **3**, 188).—The author has examined Borcher's cuprous chloride carbonic oxide cell, using carbon electrodes dipping respectively into solutions of cupric chloride in water, and of cuprous chloride in aqueous hydrochloric acid; a porous diaphragm separated the two solutions, chlorine being passed into the cupric, and carbonic oxide into the cuprous solution. After a time, the current rapidly diminished, and it was found that the cuprous chloride was completely oxidised. The carbonic oxide had taken no part in the change; of 1950 c.c. used in one experiment, 10 c.c. only were oxidised to carbonic anhydride. Similar results were obtained with electrodes of platinum, palladium, or nickel at various temperatures.

A gas battery consisting of two pieces of platinum gauze, separated by a sheet of filter paper moistened with the solution of an electrolyte, had a very low resistance, and gave encouraging results with coal gas and air, oxygen and hydrogen, or chlorine and hydrogen. The last combination, with the gases under a pressure of about 3 atmospheres, gave a current of about 1 ampère at 1·5 volts. Owing to the cost of the platinum, such a cell could not be a commercial success, but fairly good results were obtained by passing sulphurous anhydride on the one hand and chlorine on the other, under pressure, into carbon tubes dipping into dilute sulphuric acid. This combination gave 0·5 volt with 1 ohm resistance in circuit, and the products are sulphuric and hydrochloric acids. With large electrodes, good results would probably be obtained with air and sulphurous acid, in which case the product would be sulphuric acid alone.

T. E.

Laboratory Electrolytic Cells. By PAUL FUCHS (*Zeit. Elektrochem.*, 1896, **3**, 223).—The author describes three electrolytic cells which are made by Kaehler and Martini. The first consists of an inverted, tubulated bell-jar containing two horizontal discs of platinum gauze which serve as electrodes. The jar is closed air-tight by an ebonite disc, and suitable openings are provided for the escape of gases and for the introduction and removal of the electrolyte. A second form is somewhat similar, except that it is cylindrical, with vertical electrodes which may be separated by a porous pot. The third form consists of several square frames of wood impregnated with oil

and two boards similarly prepared. These may be bolted together so as to form a closed vessel. The object of this construction is to allow of electrodes or diaphragms being fixed across the box in convenient positions by clamping their edges between the frames. T. E.

Use of Porous Carbon Cylinders in Electrolytic Experiments. By WALTHER LÖB (*Zeit. Elektrochem.*, 1896, **3**, 185).—The results obtained may be summarised as follows. A carbon cylinder, when used in place of a porous earthenware cylinder, acts simultaneously as a porous diaphragm and as an intermediate conductor, one side of it acting as an anode the other as a cathode.

When such a cylinder is used as an electrode, its whole surface is active both within and without, the ions separating in the order of the facility with which they part with their charges whether they are inside or outside the cylinder. If one of the electrodes is placed in metallic contact with the cylinder, the whole system acts as an electrode. T. E.

Electrolytic Conductivity of Dilute Gases. By EILHARD WIEDEMANN and GERHARD C. SCHMIDT (*Ann. Phys. Chem.*, 1897, [ii], **61**, 737—747).—A discharge was passed through hydrogen chloride gas, and also through the vapours of the haloid salts of mercury, under such conditions that the products appearing at the two electrodes could be collected and examined. The experiments point conclusively to the view that the conductivity of dilute gases is not electrolytic, for in some cases the products of the decomposition do not separate on the electrodes, and in others they appear in amounts quite different from those required by Faraday's law. H. C.

Specific Electric Conductivities and Freezing Points of Solutions of Water in Formic Acid. By VLADIMÍR NOVÁK (*Phil. Mag.*, 1897, [v], **44**, 9—20).—Owing to the ease with which formic acid absorbs water, and the rapidity with which the resistance of the strong acid changes, it was not found possible to determine the conductivity of the anhydrous acid. With solutions containing from 0·58 to 24 per cent. of water, however, the conductivity was determined at several temperatures, and the value at the freezing point of the solution obtained by extrapolation. It is found, if these values be taken as ordinates and the freezing temperatures as abscissæ, that the points, with the exception of those for the three lowest concentrations, fall upon a straight line of which the equation is $c = 64{\cdot}77 - 6{\cdot}937t$. The specific conductivity of the anhydrous acid cannot be obtained from this equation, but as calculated by extrapolation from the three lowest concentrations, the value $1{\cdot}5 \times 10^9$ at 8·52° (in terms of mercury at 8·52°) is obtained, a result in accord with experiments of Saposchnikoff. The depression of the freezing point is also proportional to the *percentage* of water, and is calculable by the equation $t = 8{\cdot}52 - 1{\cdot}537p$, from which it is clear that the molecular depression is only constant at low concentration. The temperature coefficient of the conductivity was found to be about 0·020 for all the solutions. L. M. J.

Electrical Conductivity of Salts in Various Solvents. By CARLO CATTANEO (*Rend. Accad. Linc.*, 1895, ii, 63—70, 73—77).—In continuation of his previous work (Abstr., 1896, ii, 231), the author has determined the electrical conductivity of a number of inorganic salts in methylic, ethylic, and amylic alcohols, acetone, acetic acid, ether, and water solutions, and arrives at the following conclusions. The electrical conductivity of aqueous salt solutions is, in general, greater than those of the corresponding alcoholic solutions, which, in turn, are greater than those of glycerol solutions, and the latter greater than those of ethereal solutions of the same concentration. The electrical conductivities of salt solutions in water, methylic, ethylic, and amylic alcohols, glycerol and acetone do not increase proportionally with the temperature, but rather more slowly; the conductivities of the ethereal solutions, however, with a few rare exceptions, increase more rapidly than the temperature. The molecular conductivity of salts in aqueous solution increases with increased dilution, and the same is true of solutions of the chlorides in alcohol or glycerol and of mercuric iodide in ethylic, methylic, and amylic alcohols, or acetone; the molecular conductivity in ethereal solution decreases, in general, with increased dilution. The temperature coefficient is greater for aqueous than for alcoholic solutions, whilst the coefficients in ethereal solution are of the same order of magnitude as in water, but of negative sign; the coefficients in glycerol solutions are high. The solvent greatly influences the molecular conductivity of a dissolved salt, but no direct relation could be established, and it is shown that the order of conductivity is not the same in the different solvents. Mercuric iodide has a greater molecular conductivity in methylic, than in ethylic, alcohol. The experimental numbers do not confirm Ostwald's dilution law, and no relation could be established between the molecular conductivity and the molecular weight, coefficient of internal friction, or dielectric constant of the various solvents. Further, it seems that the ionic velocities are not wholly independent of the nature of the solvent.

W. J. P.

New Physical Method of Determining Constitution. By PAUL DRUDE (*Ber.*, 1897, 30, 940—965).—The extent to which rapidly oscillating electrical vibrations are absorbed during their passage through chemical substances, is highly characteristic of the constitution of the latter, and can be used for determining it. Conductors are electrically absorbent, and the absorption decreases as the electrical vibrations become more rapid; with 4×10^8 vibrations per second, the electrical absorption of water is negligably small, whilst that of aqueous copper sulphate can be detected in solutions of more than 0·5 per cent. concentration. This so-called "normal" electrical absorption which accompanies conduction is negligable in organic compounds. Electrical vibrations of high frequency are strongly absorbed by the alcohols, amylic alcohol being as strongly absorbent as an aqueous solution of 20,000 times the conductivity; this the author ascribes to "abnormal" electrical absorption, and finds that, whilst the normal absorption decreases as the frequency of vibration increases, the abnormal electrical absorption increases with the speed of vibration. All the

alcohols are strongly absorbent to vibrations of 4×10^8 per second, but the isomeric ethers are non-absorbent; the conclusion is therefore drawn that, with the exception of water, all liquids containing hydroxyl show abnormal electrical absorption, whilst those containing no hydroxyl are in general non-absorbent. Phenyl ethyl ketone and monobromonaphthalene are slightly absorbent, and the behaviour of these substances and of water are the most notable exceptions to the general rule; the apparently anomalous behaviour of a number of the ketones examined is probably due to tautomerism. Abnormal electrical absorption is shown by concentrated solutions of many hydroxylic compounds, such as sugar; in aqueous solution, acetaldehyde shows considerable electrical absorption.

Although the method now described affords no certain means of identifying hydroxylic compounds, it may, in doubtful cases, prove a valuable guide. The method and apparatus employed will be described at length in a later paper; only about 0·75 c.c. of material is required.

W. J. P.

Conductivity of Carbon for Heat and Electricity. By L. Cellier (*Ann. Phys. Chem.*, 1897, [ii], 61, 511—526).—Four specimens of carbon were examined:—I. Graphite of density 1·698. II. Electric light carbon of density 1·467. III. Ditto of density 1·567 IV. Gas retort carbon of density 1·627. The results are given in the following table, in which T is the temperature, K_w the heat conductivity, K_e the electrical conductivity, and c_1 the specific heat for unit volume.

	T.	c_1.	K_w.	K_e.	K_w/K_e.
I.	6·84°	0·3055	0·701	$13·049 \times 10^{-9}$	$53·72 \times 10^6$
II.	9·04	0·2488	0·367	$146·32 \times 10^{-9}$	$2·509 \times 10^6$
III.	7·83	0·2667	0·494	$267·88 \times 10^{-9}$	$1·844 \times 10^6$
IV.	9·04	0·2782	0·400	$185·36 \times 10^{-9}$	$2·158 \times 10^6$

Weber has shown that for the metals, $K_w/K_e = a + bc_1$, where $a = 5·28 \times 10^4$ and $b = 8·19 \times 10^4$. It is evident that this relationship does not hold in the case of carbon, and that the heat conductivity is 15 or 20 times greater than would be looked for in a metal. H. C.

Comparison of Rowland's Mercury Thermometers with a Griffiths' Platinum Thermometer. By C. W. Waidner and F. Mallory (*Phil. Mag.*, 1897, [v], 44, 165—169).—The values for the mechanical equivalent of heat obtained by the mechanical and electrical methods differ by an amount too great to be ascribed to experimental errors. The authors, therefore, compared the mercurial thermometers employed by Rowland with a Griffiths platinum thermometer, the comparison of which with the air scale has been carefully investigated by Callender and Griffiths (Abstr., 1891, 1146). Curves are added giving the corrections to be applied to Rowland's thermometers to reduce the readings to the air scale. These corrections are, however, insufficient to account for the difference in the values of the mechanical equivalent. L. M. J.

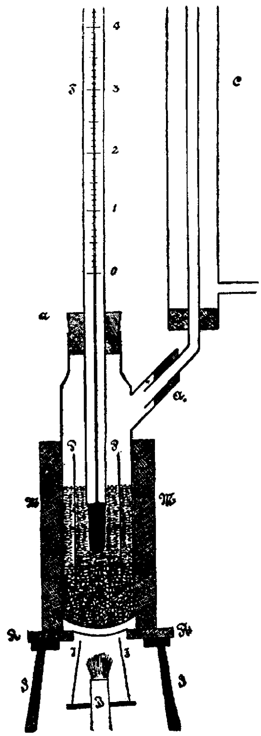
A Recalculation of Rowland's Value of the Mechanical Equivalent of Heat in Terms of the Paris Hydrogen Thermometer. By W. S. DAY (*Phil. Mag.*, 1897, [v], **44**, 169—172).—The thermometers used by Rowland were compared with three thermometers which had themselves been carefully compared with the hydrogen scale of the International Bureau of Weights and Measures. As, in the comparison, the thermometers were placed horizontally, whereas they were used vertically by Rowland, corrections for compressibility had to be applied. The values for the mechanical equivalent thus obtained are given below.

Temperature.	Old value.	Corrected value.	Electrical method.
6°	$0·4209 \times 10^4$	$0·4204 \times 10^4$	
15°	$0·4189 \times 10^4$	$0·4189 \times 10^4$	$0·4199 \times 10^4$
25°	$0·4173 \times 10^4$	$0·4177 \times 10^4$	$0·4187 \times 10^4$
35°	$0·4173 \times 10^4$	$0·4174 \times 10^4$	

The corrected values still differ considerably from those obtained electrically; this the author considers to be due to errors in the electrical standards. L. M. J.

Boiling-point Apparatus for use with Solvents of Low and High Boiling-point. By HARRY CLARY JONES (*Amer. Chem. J.*, 1897, **19**, 581—597).—The apparatus consists of a boiling-vessel, A, of much the usual form, 18 cm. long by 4 cm. in diameter, closed at the bottom, and cylindrical in shape, but narrowing to about $2\frac{3}{4}$ cm. at the neck, which is ground to receive a glass stopper; just below the shoulder there is a side tube, *a*, 2—$2\frac{1}{4}$ cm. in diameter; to this the condenser, *c*, which is about 40 cm. long, is attached by means of a cork. Up to this side tube, the vessel is surrounded by a close-fitting mantle, *m*, 12 cm. high by $1\frac{1}{2}$ cm. thick; this consists of an inner layer of thin asbestos-cardboard secured with copper wire, round which thick asbestos paper is wrapped until the desired thickness is attained. The apparatus stands on an asbestos ring, R, supported on a tripod, S; this ring is about 9 cm. in external diameter, and has in the centre a circular hole, about $3\frac{1}{2}$ cm. in diameter, over which a piece of fine copper gauze is placed; the glass bottom of the boiling vessel rests on this gauze, and is heated by a Bunsen burner underneath. The bottom of the vessel is filled with glass beads; down into these, to the depth of $\frac{1}{2}$—1 cm., is pushed a platinum cylinder, P, 8 cm. high by $2\frac{1}{2}$ cm. wide; this can be made simply by rolling up a piece of platinum foil and fastening it, but it is better that the edges should be welded. Inside the cylinder, and on the top of the glass beads, are placed some pieces of platinum foil about $\frac{3}{4}$ cm. square and with the corners bent alternately up and down. In the actual experiment, the bulb of the thermometer is situated within the cylinder, and so has platinum all round it, and below; this prevents radiation. Further, the apparatus is never filled to such a level that the liquid in it can boil over the top of the platinum cylinder; the cooled solvent flowing back from the condenser

cannot thus come into direct contact with the thermometer, but has first to pass down and up through the beads, by which process it is heated to the proper boiling point of the solution. These are the two distinctive points of the apparatus, and to them is attributed the fact that it gives more concordant results than other forms.



In making an experiment, the stopper is placed in the neck of the vessel, the side tube is closed with a cork, and the whole is weighed. A suitable quantity of solvent is then introduced, and the whole reweighed. The stoppers are then removed, the condenser is inserted into the side tube, and the Beckmann thermometer, by means of a cork, into the neck of the vessel, and the boiling point of the solvent is determined in the usual way. Some of the substance to be experimented with, in the form of pellets, is shaken from a tared tube into the apparatus, either through the condenser, or through the neck if the solvent is but little volatile; and the boiling point is again determined. Great care must be taken that the liquid boils quietly but very actively; boiling of an explosive character must be avoided. A small hand lens should be used in reading the thermometer and the latter should be tapped once or twice with a pencil just before the temperature is read. The time that elapses before the thermometer becomes stationary is much greater in the case of the pure solvent than in that of the solution.

In the results quoted below, each pair of numbers represents a series of determinations of the molecular weight, the numbers quoted being the lowest and highest values obtained. The names of the solvents are printed in italics, those of the dissolved substances in ordinary type; the true molecular weights are printed in brackets.—*Ether;* naphthalene (128): 126·9—128·8, 126·5—126·9. *Alcohol*; NHPh·P(NPh)$_2$ (305): 298—306. *Benzene*; naphthalene: 133·0—135·4, 133·7—137·4, 133·0—134·0, 135·1—136·4. *Anisoil*; acetanilide (135): 173·0—176·7, 170·4—179·4; *anthracene* (178): 201·0—205·1 198·7—207·9. *Aniline*; triphenylmethane (244): 238·6—247·4, 237·0—242·6; diphenylamine (169): 167·1—174·1. C. F. B.

Thermochemistry of Copper Compounds. By PAUL SABATIER (*Compt. rend.*, 1897, **125**, 301—305).—Anhydrous cupric oxide readily soluble in acids is obtained by heating at 440°, for 7 or 8 hours, the brown hydroxide obtained by precipitation at 100°. The difference between the heat of dissolution in acids of this oxide and that obtained by strongly heating is +2·0 Cal.

The heat of neutralisation of the oxide, corrected for the thermal disturbance resulting from the action of dilute acids on solutions of cupric salts are,

		Hydroxide	
	Dried Oxide	Brown	Blue
Nitric acid...........	16·2 Cal.	16·4 Cal.	15·9 Cal.
Hydrochloric acid ...	16·4 „	16·6 „	16·1 „
Hydrobromic acid ...	16·1 „	16·3 „	15·8 „
Sulphuric acid	19·2 „	19·4 „	18·9 „

These results show that CuO dried $+ \frac{1}{4}H_2O$, solid $= \frac{1}{4}Cu_4H_2O_5$ develops $-0·5$ Cal., and CuO, dried $+ H_2O$, solid $= Cu(OH)_2$ develops $-1·1$ Cal.

The heat of dissolution of the nitrate, $Cu2NO_3 + 6H_2O$, was found to be $-10·5$ Cal. at about 15°, and since that of the hydrate $Cu2NO_3 + 3H_2O$ is $-2·5$ Cal. (Thomsen) it follows that $Cu(NO_3)_2,3H_2O + 3H_2O$ solid $=$ $Cu(NO_3)_2,6H_2O$ develops $+3·9$ Cal. $(1·3 \times 3)$

The hexahydrate loses half its water by efflorescence, and this agrees with the author's previous observation that many chlorides lose by efflorescence any water of hydration the heat of combination with which is lower than 2·0 Cal.

The following numbers were obtained for the heat of dissolution of the basic salts in the corresponding dilute acids; basic nitrate + 34·0 Cal., basic sulphate + 48·0 Cal., basic bromide + 32·4 Cal., and the following results can be deduced.

$Cu(NO_3)_2 + 3CuO$ dried $= Cu(NO_3)_2,3CuO$ develops $+ 14·6$ Cal.
$Cu(NO_3)_2,3H_2O$, solid $+ 3CuO$ dried $= Cu(NO_3)_2, 3Cu(OH)_2$ develops $+ 12·1$ Cal.
$CuSO_4$ diss. $+ 3Cu(OH)_2 = CuSO_4,3CuO,4H_2O$, develops $+ 5·9$ Cal.
$CuSO_4,H_2O$ cryst. $+ 3Cu(OH)_2 = CuSO_4,3CuO,4H_2O$, develops $+ 15·2$ Cal.
$CuBr_2$ diss. $+ 3Cu(OH)_2 = CuBr_2,3Cu(OH)_2$, develops $+ 14·2$ Cal.
$CuBr_2$, solid $+ 3Cu(OH)_2 = CuBr_2,3Cu(OH)_2$, develops $+ 22·2$ Cal.

The heat of dissolution of anhydrous cupric bromide is $+7·9$ Cal. at 12° and $+8·8$ Cal. at 24°.

It will be observed that, except in the case of the sulphate, the heat of formation of the basic salts is considerable. The smaller development of heat in the case of the sulphate agrees with the known fact that basic sulphates containing lower proportions of oxide can be prepared.

C. H. B.

Thermochemistry of Mercury Salts. By RAOUL VARET (*Ann. Chim. Phys.*, 1896, [vii], 8, 79—141).—In the first chapter of this memoir, dealing with compounds of mercury with the elements, the heats of formation of mercurous and mercuric chlorides, bromides, iodides, and oxides are given (Abstr., 1895, ii, 305, 380, 381). The following heat of formation of mercuric sulphide is recorded :—Hg liq. + S sol. = HgS ppt. develops + 10·6 Cal. Numbers representing the thermal disturbances accompanying the isomeric change of mercuric sulphide are also given (Abstr., 1895, ii, 435). The second chapter deals with the thermochemistry of mercuric sulphate, basic mercuric sulphate (Abstr., 1895, ii, 103), and mercurous sulphate (Abstr., 1895, ii, 380). For mercurous sulphate, the following additional numbers are given.

Hg_2O sol. + SO_3 sol. = Hg_2SO_4 sol. develops + 49 Cal.
Hg_2O sol. + H_2SO_4 diss. = Hg_2SO_4 sol. + H_2O liq. develops + 11·8 Cal.
Hg_2O sol. + H_2SO_4 liq. anhyd. = Hg_2SO_4 sol. + H_2O liq. dev. + 28·8 Cal.

The third chapter deals with the nitrates of mercury, the heats of formation and of dissolution of mercuric nitrate and basic mercuric nitrate being given (Abstr., 1895, ii, 154), as also those of mercurous nitrate (Abstr., 1895, ii, 380). For the latter salt, the following additional numbers are recorded.

Hg_2O sol. + $3HNO_3$ diss. = $Hg_2(NO_3)_2$ diss. + HNO_3 diss- + H_2O liq. dev. + 6·23 Cal.
Hg_2O sol. + $2HNO_3$ diss. = $Hg_2(NO_3)_2,2H_2O$ sol. develops + 18·63 Cal.

The fourth chapter contains an account of the preparation, properties, and thermochemistry of mercuric picrate (Abstr., 1895, i, 131) and of mercurous acetate (Abstr., 1895, ii, 381). The following additional observations are recorded.

Hg_2O sol. + $2C_2H_4O_2$ diss. = $Hg_2(C_2H_3O_2)_2$ sol. + H_2O liq. dev. + 14·73 Cal.
Hg_2O sol. + $2C_2H_4O_2$ sol. = $Hg_2(C_2H_3O_2)_2$ sol. + H_2O liq. „ + 11·93 Cal.
Hg liq. + $Hg(C_2H_3O_2)_2$ sol. = $Hg_2(C_2H_3O_2)_2$ sol. „ + 5·20 Cal.

A. C. C.

Isothermals of Isopentane. By J. Rose-Innes (*Phil. Mag.*, 1897, [v], **44**, 76—82).—The experiments of Young (*Proc. Phys. Soc.*, 1894, 602) give a complete series of isothermals for isopentane, and the author endeavoured to find a suitable equation to represent these curves. Making use of Ramsay and Young's relation that $p = bT - a$ at constant volume, it is evident that $pv = RT$ only at temperature $T = a(b - R/v)$. This temperature is, however, seen from Young's results to be practically constant for a very large range of volumes, namely, from 8 to 350. Confining the investigation to volumes above 3·4, the author finds the values $a = l \div v(v + k)$ and $b = R/v \times \{1 + e \div (v + k - g/v^2)\}$ give satisfactory results where l, k, e, and g are constants whose values are given. From the equation thus obtained, by determining the value of v where dp/dv and d^2p/dv^2 vanish, the critical volume is obtained, and hence the critical temperature and pressure. The numbers calculated in this way are critical vol. = 4·5, critical temp. = 191·7°, critical pressure = 26250; these agree satisfactorily with the experimental results obtained by Young.

L. M. J.

Melting Points of Organic Substances. By Antoine P. N. Franchimont (*Rec. Trav. Chim.*, 1897, **16**, 126—161).—From a careful and detailed study of the relations existing between the composition of substances and their melting points, the author deduces certain rules, to which, however, there are many exceptions, but doubtless a number of these will disappear on closer investigation.

In general, the melting point of an organic compound *increases* (*a*) when two atoms of hydrogen connected to the same carbon atom are replaced by an atom of oxygen; (*b*) when an atom of hydrogen is replaced by the groups OH or NH_2; (*c*) when 3 atoms of hydrogen connected to the same carbon atom are replaced by a nitrogen atom; and *decreases* when an atom of hydrogen connected to an oxygen or

carbon atom, or a hydrogen atom of an NH_2 group, is replaced by the group CH_3. In the case of hydrogen, connected to a carbon atom, or in an NH_2 group, this is only strictly true of the first atom replaced; for although carbamide melts at 132° and methylcarbamide at 102°, the dimethyl derivative melts at 180°.

By introducing a CH_3 group into a compound, the symmetry of the latter is more or less altered, and this fact has a great influence on the melting point. For example, in malonic acid, the symmetry is modified by the introduction of one CH_3 group, and is re-established by a second, as is seen from the following.

$$\begin{array}{ccc} H & & COOH \\ & C & \\ H & & COOH\ (134°) \end{array} \qquad \begin{array}{ccc} CH_3 & & COOH \\ & C & \\ H & & COOH\ (130°) \end{array} \qquad \begin{array}{ccc} CH_3 & & COOH \\ & C & \\ CH_3 & & COOH\ (180°). \end{array}$$

The effect on the melting point is a lowering in the first place but an increase in the second, and this effect is more marked when an ethyl or higher alkyl group is substituted for hydrogen; ethylmalonic acid melts at 111·5° and the diethyl derivative at 125°. It is evident, therefore, that by the partial re-establishment of the symmetry of a compound, its melting point is increased.

In 1872, the author, in conjunction with Zincke, pointed out that nonylic acid melts at a lower temperature than octoic acid, so that in a homologous series the melting point is not always augmented with increase in carbon; and the possibility was suggested that acids containing an even number of carbon atoms have a relatively higher melting point than those with an uneven number. A similar fact is noticeable in the case of the normal aliphatic hydrocarbons, where in passing from a hydrocarbon with an even number of carbon atoms to the next higher homologue with an uneven number, the melting point does increase, but to a much less degree than in passing from a hydrocarbon with an uneven number of carbon atoms to the next higher member with an even number. It is not certain if this phenomenon is general among normal aliphatic compounds, although it would appear probable, as it is not limited to the above examples. Symmetry here again plays an important part, for in compounds with an even number of carbon atoms (and higher melting point), the symmetry is more perfect than in those with an uneven number of carbon atoms, if a molecule is considered as consisting of two equal parts which have a symmetry with regard to a plane dividing the molecule in half.

Concerning the effect produced on the melting point of a substance when a CH_2 group replaces two hydrogen atoms attached to the same carbon atom or CH replaces three hydrogens, facts which throw any light on the subject are almost totally wanting. In unsaturated hydrocarbons derived from saturated ones by replacement of two hydrogens of a CH_3 group by CH_2, it is noticed that the melting point decreases, and where the unsaturated is derived from the saturated hydrocarbon by the replacement of three hydrogens of a CH_3 group by CH, the melting point increases.

The substitution of one hydrogen atom by chlorine, bromine, or iodine lowers the melting point, those cases in which an elevation has been observed being exceptional, and, probably, symmetry again plays

an important part. More than one halogen atom increases the melting point, and if the entering atoms are attached to different carbon atoms the relative distance has an effect.

The entrance of such groups as NO, NOH, or NO_2 into a compound usually produces an increase in the melting point. A. W. C.

Condensation and Critical Phenomena of some Substances and Mixtures. By J. P. Kuenen (*Phil. Mag.*, 1897, [v], **44**, 174—199).—A continuation of the author's previous paper on the critical phenomena of ethane and nitrous oxide (Abstr., 1896, ii, 10). The critical values obtained for the ethane (32·05° and 48·8 atms.) differ from those previously obtained by other observers, and the author therefore investigated the purity of ethane produced by various methods. He considers it impossible to obtain pure ethane by the reduction of ethylic iodide, and finds that the purest gas is obtained by the electrolysis of sodium acetate, using Murray's method (Trans., 1892, 10).

According to Dewar (Abstr., 1880, 843), the critical temperature of a mixture of equal parts of carbonic anhydride and acetylene is higher than that of either of the constituents, but this result is found to be incorrect, and was due to an impurity in the acetylene. The author finds the critical temperature and pressure of carefully purified acetylene to be 35·25° and 61·02 atmospheres respectively, and for the mixture the critical temperature lies between those of the constituents. In the case of mixtures of ethane and acetylene, the critical temperature attains a minimum value for the mixture containing 0·53 ethane with 0·47 acetylene, which is also very nearly the mixture possessing a maximum vapour pressure. Retrograde condensation of the first kind was also well observed in these mixtures. In the case of ethane and carbonic anhydride, the minimum critical temperature occurs for 0·45 ethane, and maximum vapour pressure for 0·30 ethane. The author applies van der Waals' equation to the case of mixtures, and, regarding the constant a_x to be given by the expression $a_x = a_1(1-x)^2 + 2a_{12}x(1-x) + a_2x^2$, with a similar expression for b_x, deduces the values a_{12} and b_{12} from the critical values of one mixture, and from these, the critical values of other mixtures, supposed to remain undivided, are calculated. L. M. J.

A New Form of Pyknometer. By J. C. Boot (*J. Amer. Chem. Soc.*, 1897, **19**, 61—62).—A great inconvenience in using the ordinary form of specific gravity bottle is that, on drying the outside or during the weighing, a portion of the liquid is liable to run out, particularly if the temperature of the room is higher than that of the liquid. The author now uses a double-walled pyknometer, in which the space between the two walls is carefully exhausted. This apparatus can be carefully dried and weighed without any liquid escaping through the capillary tube. L. de K.

Contraction of some Organic Compounds on Solidification. By Adolf Heydweiller (*Ann. Phys. Chem.*, 1897, [ii], **61**, 527—540). —The contraction taking place on the solidification of benzene, phenol, menthol, thymol, stearic acid, and naphthalene was directly measured

in a dilatometer. The differences in the specific volumes of the liquid and solid $v_f - v_s = \Delta v$ were as follows:—For benzene at 5·35°, between 0·1219 and 0·1304; for phenol at 40·80°, between 0·0461 and 0·0540; for menthol at 41·37°, between 0·0485 and 0·0653; for thymol at 49·41°, between 0·0572 and 0·0709; for stearic acid 0·1387 at 67·78°; and for naphthalene at 79·86°, between 0·1241 and 0·1454. H. C.

Volume of Vapour produced from One Cubic Centimetre of a Liquid at the Boiling Point. By J. A. GROSHANS (*Ann. Phys. Chem.*, 1897, [ii], **61**, 780—789).—The volume of vapour produced from 1 c.c. of a liquid at the boiling point T in absolute temperature is given by $81·78 \times T/MV$, where MV is the molecular volume of the liquid. For compounds of similar composition, this quantity is practically constant, but varies in the case of compounds belonging to the same homologous series. These variations are, however, accounted for by the author on the basis of his previously published work on homologous compounds. H. C.

Reciprocal Diffusion of Electrolytes in Dilute Aqueous Solutions. By U. BEHN (*Ann. Phys. Chem.*, 1897, [ii], **62**, 54—67).—The author determines the relative amounts of the ions which diffuse across the boundary between two dilute solutions of one or more binary electrolytes. As cases of electrolytes in solutions of equal concentration, the two combinations of HCl—LiCl and HNO_3—$AgNO_3$ were selected. These were taken in decinormal solutions. Diffusion under the influence of a fall in concentration was studied more especially with solutions of silver nitrate containing free nitric acid. The theories of hydro-diffusion developed by Nernst and Planck were applied to the results, but no satisfactory agreement obtained, a fact which the author ascribes to the impossibility of sufficiently preventing the formation of currents in the solutions. H. C.

Diffusion Coefficients of Sodium Chloride Solutions of various Concentrations. By L. MARINI (*Rend. Accad. Linc.*, 1895, ii, 135—139).—Using a spectrometric method somewhat similar to that proposed by Wiener (*Ann. Phys. Chem.*, 1893, [ii], vol. 49), the author has determined the diffusion coefficient of sodium chloride in 2N, N, N/2, and N/5 aqueous solutions as 1·109, 1·078, 1·065, and 1·069 at 18° respectively. W. J. P.

The Ionising Power of Solvents. By W. C. DAMPIER WHETHAM (*Phil. Mag.*, 1897, [v], **44**, 1—9).—The ionising power of a solvent was shown by Nernst to be intimately connected with its dielectric constant (Abstr., 1894, ii, 266). Of all liquids hitherto examined, water possesses the highest dielectric constant and the greatest ionising power, but the author hoped that, by examining solutions of water in other liquids, indication of its dissociation might be obtained. Determinations were made of the resistances of various solutions of water in formic, acetic, and trichloracetic acids, and it is noticeable that, of these solvents, formic acid alone possesses a dielectric constant approaching that of water ($K = 62$; $K_{H_2O} = 75·5°$, Thwing). Curves of conductivity against percentage of water are given, which show that, in the acetic and trichloracetic acid solutions, the forms of the

ascending and descending portions are totally different; the former, that is the curve for the solution of water in acid, cutting the conductivity axis at right angles and ascending rapidly when the concentration reaches 10 to 20 per cent. With formic acid, on the other hand, the ascending portion is a straight line to 60 per cent. of water, and although it does not resemble the descending part, it shows that even dilute solutions of water in formic acid have considerable conductivity. The author considers that these solutions are essentially different from normal electrolytic solutions, and hence that the water is not dissociated, a view confirmed by cryoscopic observations. The conductivity of the formic acid solutions, however, renders it probable, in the author's opinion, that, in a solvent of higher dielectric constant, the water itself would be dissociated. L. M. J.

Affinity Constants and Heat of Dissociation of some Nitrogen Acids. By E. BAUR (*Zeit. physikal. Chem.*, 1897, **23**, 409—416).—Jahn found that the affinity constant of the first five fatty acids increases by about 5 per cent. between 10° and 40°, whilst Euler's results show that that of the aromatic carboxy-acids increases by about 10 per cent. between 0° and 50°. As, however, some nitrogen compounds appear to have a greater variability, the author determined the constant for nitrocarbamide, $NH_2\cdot CO\cdot NH\cdot NO_2$, nitrourethane, $EtO\cdot CO\cdot NH\cdot NO_2$, amidotetrazole, $CN_4H\cdot NH_2$, benzenesulphonitramine, $C_6H_5\cdot SO_2\cdot NH\cdot NO_2$, and their sodium salts. The conductivity was measured at 0°, 10°, 20°, 30°, 40° and 50° at various dilutions, and the affinity constant for each temperature calculated by Ostwald's formula. The benzene sulphonitramine, however, was so strongly dissociated at 0°, that no further determinations were taken. In each case investigated, the temperature coefficient was very great, the constant increasing to the extent of 85 per cent. for 20° in the case of nitrocarbamide and by 100 per cent. and 200 per cent. respectively for 40° in the cases of nitrourethane and amidotetrazole. If this high temperature coefficient should prove to be characteristic of compounds in which the acidic hydrogen is united to nitrogen, it might prove of service in the determination of constitution. The heat of dissociation of the compounds was also determined by Nernst's equation with the following results.

	Nitrocarbamide.	Nitrourethane.	Amidotetrazole.
5°	5477 cal.	3665 cal.	4724 cal.
25°	3640 ,,	2943 ,,	4593 ,,

L. M. J.

Relation between the Polymerisation of Liquids and their Power of Dissociating Electrolytes. By PAUL DUTOIT and EMILY A. ASTON (*Compt. rend.*, 1897, **125**, 240—243).—All the solvents which yield solutions having a high electrical conductivity contain the hydroxyl group, but these are also the compounds which, according to the results obtained by Ramsay and Shields, and other evidence, are

polymerised in the liquid state. The authors have determined the electrical conductivity of solutions of several metallic salts and organic acids in propionitrile, acetone, methyl ethyl ketone, methyl propyl ketone, and nitroethane, which are not hydroxyl derivatives, but yet are shown by evidence of various kinds to be polymerised in the liquid state. In all cases, the conductivites are high, and these results, when compared with the low conductivities observed by Kablukoff in solutions of electrolytes in non-polymerised solvents, seem to show clearly that there is a general relation between the dissociating power of a solvent and its polymerised or non-polymerised condition, as the case may be. C. H. B.

Decomposition of Silver Salts by Pressure. By J. E. Myers and Ferdinand Braun (*Phil. Mag.*, 1897, [v], **44**, 172—173).—It has been shown by Carey Lea that silver salts may be decomposed by pressure (Abstr., 1894, ii, 85), and the authors determined the electromotive force developed when this decomposition is effected between silver and platinum electrodes. The pressure employed was about 3000—5000 atmospheres, and the E.M.F. was found to attain a maximum value varying with the salt, and being approximately: silver bromide, 0·07; silver chloride, 0·03; and silver iodide, 0·04; the values being given in terms of the E.M.F. of a Daniell's cell. Silver nitrate and potassium bromide were not affected singly, but together gave an E.M.F. of about 0·08. The resistance also increased considerably during the compression. L. M. J.

Decomposition of Triglycerides by Bases and Dilute Acids. By Adolf C. Geitel (*J. pr. Chem.*, 1897, [ii], **55**, 429—456).—By the application of the law of mass action to the decomposition of triglycerides by bases and acids, the author arrives at the conclusion that the decomposition, and therefore the formation, of these compounds takes place in stages, the reactions being all bimolecular in the sense of the equations,

$$C_3H_5(OH)_3 + HAc = C_3H_5(OH)_2Ac + H_2O,$$
$$C_3H_5(OH)_2Ac + HAc = C_3H_5(OH)Ac_2 + H_2O,$$
$$C_3H_5(OH)Ac_2 + HAc = C_3H_5Ac_3 + H_2O.$$

In order to apply the law of mass action to each of the separate reactions in the mixture, a full mathematical consideration of the case is entered on, this necessarily taking a somewhat complex form.

H. C.

Inversion of Sugar by Salts. By John H. Long (*J. Amer. Chem. Soc.*, 1896, **18**, 693—717).—This is a continuation of the work previously described (Abstr., 1896, ii, 414). A 20 per cent. solution of sugar was mixed with varying quantities of each salt and heated at 85°, the progress of the inversion being polarimetrically determined at intervals. The results show that, with most of the salts, the inversion coefficient varies with the time. In the case of alum, it is constant throughout; with ferrous sulphate, ferrous ammonium sulphate, zinc sulphate, and cadmium chloride, it increases slowly; with manganous sulphate, manganous chloride, and lead nitrate it increases

rapidly; whilst with ferrous chloride, ferrous bromide, and ferrous iodide, it decreases rapidly. This irregular behaviour probably bears some relation to the stability of the salts in aqueous or weak saccharine solutions. The solutions of the last three salts become turbid at first but clear afterwards, whilst in the solutions of ferrous sulphate and ferrous ammonium sulphate the turbidity is persistent. Manganous sulphate is also slightly decomposed and the decomposition increases with time and temperature. The solutions with manganous chloride, cadmium chloride, and lead nitrate remain clear, but the first soon loses its pink colour and this is not restored on cooling. Here obviously some change in the form of combination of the manganese has taken place and probably in most cases formation of compounds of the base with the sugar interferes with the regularity of the rate of inversion. E. W. W.

Washing Bottle for Gases. By SEBASTIANO FAMULARI (*Gazzetta*, 1897, **27**, ii, 58—59).—This is a description of a simple washing bottle for gases in which the author states that the gas is caused to pass twice through the same washing liquor.

W. J. P.

Inorganic Chemistry.

The Commencement of the Combination of Hydrogen with Oxygen. By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1897, **125**, 271—275).—The author has made experiments with a view of ascertaining the exact nature of the influence exerted on the combination of oxygen and hydrogen by the walls of the vessel in which the gaseous mixture is contained. In all cases, the hydrogen and oxygen were mixed in the proportion of 2 volumes of the former and 1 volume of the latter. In contact with dry barium oxide, there is no combination at the ordinary temperature, nor at 100° or 182°; but at 250°, 77 per cent. of the gaseous mixture disappeared in 5 hours, and at 280°, the whole of the gas disappeared after 26 hours. Further experiments showed, however, that at first the oxygen disappears more rapidly than the hydrogen, part of it combining with the barium oxide to form the peroxide, which is subsequently reduced by the hydrogen. At 280°, for example, all the oxygen disappeared after 5 hours, but 16 per cent. of the hydrogen remained; the latter was, however, gradually absorbed. The influence of the barium oxide is of the same order as that exerted by platinum.

Potassium hydroxide behaves similarly, combination taking place slowly at 250°, and somewhat rapidly at 280—300°. The glass is somewhat strongly attacked and alkali manganates derived from the manganese in the glass are formed. In this case, also, the oxygen at first disappears more rapidly than the hydrogen, owing to the formation of peroxides and manganates.

Direct experiments show that in presence of a very small quantity of water, glass absorbs relatively considerable quantities of oxygen, but no such absorption takes place with a larger proportion of water.

The intermediate formation of alkali peroxides no doubt plays an important part in the combination of hydrogen and oxygen when heated in glass vessels. C. H. B.

Electrolytic Formation of Persulphuric Acid. By FRANZ RICHARZ (*Ber.*, 1897, **30**, 1826—1827).—*Apropos* of Nernst's lecture (this vol., ii, 394), the author recalls the fact that already in 1884—1888, he had investigated and explained the above reaction. He has also shown (Abstr., 1896, ii, 585) that, with dilute sulphuric acid, the attainment of a potential difference of 1·08 volts. is characterised, not only by a sudden rise in the strength of the current (as was observed long ago by Helmholtz), but also by the setting-in at the cathode of the formation of hydrogen peroxide by reduction of dissolved neutral oxygen. C. F. B.

Atomic Weights of Nitrogen, Chlorine, and Silver. By ANATOLE LEDUC (*Compt. rend.*, 1897, **125**, 299—301).—Taking $O = 16$ and $C = 12·004$, the author's determinations of the sp. gr. of gases, combined with the fact that the molecular volume of nitrogen is higher than that of carbonic oxide (*Compt. rend.*, **125**, 297), lead to the conclusion that $N = 14·005$. Stas found $N = 14·044$, but if his results are corrected for the oxygen probably present in the silver used, the number becomes $N = 14·002$. Adopting the author's value for N, the ratio $Ag : NO_3$ is 1·7404, whereas the later experiments of Stas give 1·7400.

The numbers finally adopted by the author are, $O = 16·00$, $N = 14·005$, $H = 1·0076$, $Cl = 35·47$, and $Ag = 107·916$. C. H. B.

The Different Varieties of Carbon (Amorphous, Graphite, Diamond). By HENRI MOISSAN (*Ann. Chim. Phys.*, 1896, [vii], **8**, 289—305, 306—347 and 466—558).—A full account is given of the methods of production, modes of occurrence, and general properties of various forms of carbon, the first of the three papers dealing solely with the element in the amorphous state. Carbon prepared by the following methods was studied, (1) by the incomplete combustion of petroleum; (2) by the incomplete combustion of acetylene; (3) by the decomposition of acetylene by detonation with mercuric fulminate; (4) by the action of sulphuric acid on starch; (5) by the action of ferric chloride on anthracene at 180°; (6) by the decomposition of carbon tetriodide at 200°; (7) by the action of light on carbon tetriodide; (8) by the action of a Smithson couple on a solution of carbon protoiodide in carbon bisulphide; (9) by the action of zinc filings on carbon tetriodide; (10) by the action of magnesium on a solution of the tetriodide in carbon bisulphide, and (11) by the action of boron at a red heat on carbonic anhydride. The carbon prepared by all these methods was amorphous and always more or less impure, its complete purification being, if not impossible, at least extremely difficult, owing to the great tenacity with which it retains water, traces of hydrocarbons, and small quantities of the elements present during its separation, such as iodine, lead, zinc, &c. Methods (4) and (5) yielded mixtures of organic compounds rich in carbon, from which it was impossible to obtain the element even moderately pure in the amorphous state. The density of amorphous carbon, by

whatever method prepared, is always less than 2, being 1·76 in the case of the purest, non-ignited lampblack. When heated, amorphous carbon undergoes polymerisation, its ignition point in oxygen being raised and its resistance to the action of chromic acid mixture increased.

The second paper deals with graphite, the first chapter containing an account of samples obtained from Ceylon, Borrowdale, Ticonderoga, Greenville, Omeansk, Mugrau, Scharzbach and Karsok (Abstr., 1896, ii, 165), from an American pegmatite (Abstr., 1896, ii, 182), and from Blue Earth from the Cape (Abstr., 1893, ii, 285). The nature of the carbon existing in meteoric irons is also discussed (Abstr., 1893, ii, 288, 475; 1896, ii, 194). In the second chapter, the rates of oxidation, the ignition points, and the densities of artificially prepared samples of graphite are given (Abstr., 1895, ii, 219), and the displacement of carbon in fused cast-iron by boron and silicon is described (Abstr., 1895, ii, 220). The properties of graphite separated from iron are also given (Abstr., 1895, ii, 220). The third chapter deals with the preparation and properties of intumescent graphite (Abstr., 1893, ii, 320; 1895, ii, 221).

In the first chapter of the third paper, the author gives the properties of the diamond and the composition of the ash left on ignition (Abstr., 1893, ii, 319); the occurrence of diamonds in the Blue Earth from the Cape, in sand from Brazil, and in the meteorite of Cañon Diablo is also discussed (Abstr., 1893, ii, 285; 1897, ii, 46; 1893, ii, 288, and 1896, ii, 194). The second chapter deals with the solubility of carbon in various metals at ordinary pressures and the formation of definite carbides (Abstr., 1893, ii, 275; 1894, ii, 452; 1895, ii, 272, 501; 1896, ii, 364, 419, 422, 423, 428, 606, 608, 609, and 650). The third chapter contains an account of the effect of high temperatures on the different forms of carbon (Abstr., 1894, ii, 42), and of the properties of its vapour (Abstr., 1895, ii, 164). In the fourth chapter, numerous experiments on the artificial production of diamonds are detailed (Abstr., 1893, ii, 275; 1894, ii, 189; 1895, ii, 644), whilst the fifth is devoted to a description of the method adopted for the combustion of artificially prepared diamonds. A. C. C.

Electrolytic Preparation of a New Class of Oxidising Substances. By EMIL J. CONSTAM and ARTHUR VON HANSEN (*Zeit. für Elektrochem*, 1896, **3**, 137).—It is to be expected that the alkali carbonates will, in very concentrated solutions, dissociate into the ions $\overset{+}{M}$ and $\overset{-}{MCO_3}$, and that the latter will unite to form percarbonates, $M_2C_2O_6$, when liberated by electrolysis at the anode. When a saturated solution of potassium carbonate is electrolysed, the evolution of oxygen diminishes as the temperature falls, ceasing almost completely at $-10°$. At the same time, the precipitate of potassium hydrogen carbonate, which at first forms at the anode, is replaced by a bluish, amorphous powder consisting of potassium percarbonate. In order to obtain a good result, the solution must be saturated and the temperature not allowed to rise above $-10°$ to $-15°$. The current density has no very marked influence on the result. The dried product is a bluish-white, amorphous, deliquescent powder, which is decomposed, when gently heated, into potassium carbonate, carbonic anhydride, and oxygen. It dissolves almost without decomposition in ice-cold water,

but is decomposed by water at the ordinary temperature. It is somewhat soluble in alcohol. It liberates iodine from a solution of potassium iodide, especially after acidification, oxidises lead sulphide to sulphate, bleaches indigo, wool, cotton, or silk, and reduces the peroxides of manganese and lead, and silver oxide, forming the corresponding carbonates and liberating oxygen. With caustic potash, or with dilute sulphuric acid, it yields hydrogen peroxide. The substance, dried over phosphoric anhydride, contains from 53·59 to 77·91 per cent. of potassium percarbonate, the remainder being potassium carbonate, bicarbonate, and water. Rubidium percarbonate was obtained in a similar way. The sodium and ammonium salts could not be obtained in the solid state owing to the comparatively small solubilities of the carbonates. T. E.

Double Halogen Salts of Cæsium and Rubidium. By HORACE L. WELLS and H. W. FOOTE (*Amer. J. Sci.*, 1897, **3**, 461—465).—The authors have prepared the rubidium antimony chloride described by Remsen and Saunders (*Amer. Chem. J.*, **14**, 155) to which they gave the formula $23RbCl,10SbCl_3$; the salt is not altered by recrystallisation under varying conditions from strong or dilute hydrochloric acid, or from a solution of hydrogen chloride in alcohol; from this the authors conclude that the substance is not a mixture of two simpler salts. The results obtained on analysis agree more closely with the formula $7RbCl,3SbCl_3$, but the differences between the two formulæ in percentage composition are so slight that it is impossible to decide between them by means of chemical analysis.

Rubidium antimony oxychloride, $2RbCl,SbCl_3,SbOCl$, is obtained when the preceding salt is crystallised from very dilute hydrochloric acid; it crystallises in short, colourless prisms.

The double chlorides of bismuth and cæsium described by Remsen and Brigham are formed under the following conditions. The salt $3CsCl,BiCl_3$, separates in colourless plates when cæsium chloride (50 grams), in hydrochloric acid solution, is mixed with bismuth chloride (1 to 25 grams). The salt, $3CsCl,2BiCl_3$, obtained when bismuth chloride (50 grams) is mixed with cæsium chloride (1 to 80 grams), crystallises in pale, yellow needles.

Cæsium bismuth iodide, $3CsI,2BiI_3$, is the only double iodide the authors were able to prepare; it is obtained under all conditions when the two iodides are mixed, and is a bright red to reddish-brown, crystalline precipitate which is only very sparingly soluble, especially in an excess of cæsium iodide. E. C. R.

Silver Peroxynitrate. By EDUARD MULDER (*Rec. Trav. Chim.*, 1897, **16**, 57—112).—Continuing his researches on the black, crystalline compound of the formula Ag_7NO_{11} (Abstr., 1896, ii, 561), the author has submitted it to the action of heat, and finds that it decomposes at a relatively low temperature, giving off oxygen. In the first series of experiments, extending over 90 days, the substance was heated in a slow current of dry air at a temperature of 52° to commence with, this temperature being gradually increased to 185°. A total loss in weight corresponding with 5 atoms of oxygen was observed, but the elimination of oxygen does not proceed regularly, apparently taking place in at least two phases. Three atoms of oxygen are lost at 51—60°, but

whereas the first disappears after 11 hours, and the second after a further 17 hours heating, the third atom requires 63 hours; the temperature has to be considerably raised before the remaining atoms are driven off.

The second series of experiments was carried out in a similar manner, more care being taken to exclude moisture, which has apparently a notable influence on the rate of decomposition of the substance; the results are much more regular than in the first case, this being probably due to the absence of moisture.

The substance, Ag_7NO_{11}, may be regarded as a molecular combination of silver peroxide, Ag_2O_2, and a silver dioxynitrate of the composition $AgNO_5$, which gives a formula $3Ag_2O_2,AgNO_5$; this is not at variance with the valencies ordinarily ascribed to its constituent elements, but presupposes the existence of the salt of an acid, HNO_5, a substance not known at present. In general, the stability of a substance containing a large number of oxygen atoms decreases with increase in oxygen, so that the spontaneous decomposition of the substance Ag_7NO_{11} would be explained by the presence of the dioxynitrate $AgNO_5$. The initial decomposition may be therefore expressed by the equation $3Ag_2O_2,AgNO_5 = 3Ag_2O_2,AgNO_3 + 2O$.

If, after elimination of two oxygen atoms, the residue is treated with water, an amount of silver nitrate is extracted corresponding with 17·8 per cent. of the original substance; the formula $3Ag_2O_2,AgNO_5$ requires 17·98 per cent. After the silver nitrate has been removed, the residue is found to resemble graphite in appearance, is comparatively stable, and has the formula $Ag_2O,5Ag_2O_2$, but is in all probability a mixture of the ordinary oxide and a silver peroxide, which does not resemble the one described by Berthelot, nor has it a red colour like that described by Iles (*Eng. and Min. Journ.*, 1884, 297). The presence of the ordinary oxide of silver may be explained by supposing that the initial decomposition already mentioned is accompanied by a secondary one, namely, the action of the oxygen liberated from the peroxynitrate on the silver peroxide, according to the equation $AgNO_5,3Ag_2O_2 = AgNO_3 + 2Ag_2O + Ag_2O_2 + 2O_2$.

On heating the peroxide, silver oxide, Ag_2O, is left, which has also the appearance of graphite, and is more stable than the ordinary variety of this oxide, not being decomposed below a temperature of 300°.

The author speculates on the possible existence of acids such as HNO_5 and HNO_4, and their corresponding anhydrides, N_2O_5 and N_2O_4.

A. W. C.

Precipitated Calcium Carbonate. By MAX ADLER (*Zeit. angw. Chem.*, 1897, **14**, 431—434).—The precipitation of calcium carbonate in the aragonite form is determined by the temperature of the solutions, the concentration, the nature of the atmosphere in which the precipitation takes place, and by the pressure. In the preparation of calcium carbonate from solutions of calcium chloride and ammonium carbonate, the temperature at which the aragonite form is converted into the calcite form is increased to a much greater extent by an increase in the concentration of the ammonium carbonate than by an increase in the concentration of the calcium chloride. Using the ammonium carbonate of such a concentration that on adding the calcium chloride

a thick, gelatinous mass is obtained, the limit of temperature for the ammonium carbonate solution is 32°, whilst the calcium chloride may be used boiling. With dilute solutions at the same temperature, the aragonite crystals are at once converted into calcite; the limit of temperature for weak solutions is 22°, and the lower the temperature the smaller and more stable are the crystals of aragonite. The presence of carbonic anhydride in the solution determines the formation of calcite, and this explains the formation of calcite when the ammonium carbonate is at a high temperature, as it is then decomposed, with the formation of carbonic anhydride. Precipitated aragonite, when subjected to a pressure of 5—6 atmospheres, is converted into calcite. The aragonite form is more stable when the solution is alkaline with an excess of ammonium carbonate, and also when the precipitate is washed with water containing calcium sulphate instead of with pure water. When the aragonite prepared from calcium chloride and ammonium carbonate is separated from the mother liquor and heated to 60°, it is converted into calcite; on the other hand, the aragonite precipitated by sodium carbonate can be heated to 100° without change. E. C. R.

Action of Cupric Hydroxide on Silver Nitrate Solutions. By PAUL SABATIER (*Compt. rend.*, 1897, **125**, 175—178).—When silver oxide is placed in a solution of an excess of cupric nitrate, the greenish-blue precipitate that forms is not copper hydroxide, as has hitherto been supposed, but is a basic cupric nitrate, $Cu(NO_3)_2,3Cu(OH)_2$. All the silver is dissolved in the form of nitrate. When the silver oxide and cupric nitrate are in equal molecular proportions, the product is a mixed basic nitrate of silver and copper, $3CuO,2AgNO_3,3H_2O$. When the silver oxide is in excess, the same product is obtained mixed with unaltered oxide.

When blue cupric hydroxide is added to silver nitrate solution, the mixed basic nitrate is obtained in microscopic needles. Neither cupric oxide nor the hydroxide $Cu_4H_2O_5$ (this vol., ii, 491) has any action on the silver nitrate solution, and if the blue hydroxide is mixed with either of them, the brown compound remains unchanged and is readily separated from the basic salt by levigation.

The basic silver copper nitrate forms blue-violet prisms, highly elongated and terminated by a base normal to the edges, or by a strongly inclined face. It is stable in dry air, but when heated loses water and decomposes into cupric oxide and silver nitrate. Hot water decomposes it at once into brown cupric hydroxide and silver nitrate, and cold water very slowly produces the same change. Cupric nitrate solution converts it into basic cupric nitrate, and the silver nitrate is dissolved. The double basic salt may be regarded as the compound $Cu(NO_3)_2,3CuO$, in which 1 atom of copper has been displaced by 2 atoms of silver, but the two basic salts are far from being isomorphous.

C. H. B.

Preparation of Thallium by Electrolysis. By FRITZ FOERSTER (*Zeit. anorg. Chem.*, 1897, **15**, 71—74).—Thallium chloride is prepared from the flue-dust of pyrites burners by precipitating the aqueous solution of the flue-dust with salt, then reconverting the product into sul-

phate and again precipitating with salt, the chloride thus obtained being heated with double the quantity of sulphuric acid necessary to convert it into the normal sulphate until copious acid fumes are given off. A saturated solution of the cold product is employed for the electrolysis. If too small an excess of sulphuric acid is present, brown thallium sesquioxide is deposited at the anode owing to the hydrolysis of thallium sulphate. The cathode consists of a circular ring of thin copper plate lying on the bottom of the glass vessel containing the electrolyte, two anodes of platinum foil being supported above it; in order to prevent short circuiting, the electrolyte is stirred by means of a glass stirrer which revolves between the anode and cathode and is driven by a fan. The stirring apparatus is similar to that employed in Ostwald's thermostat. A current density of 1·3—1·5 ampère per square decimetre and a potential difference of 3·5 volts. is employed; 30—50 grams of thallium chloride are then electrolysed in about 3 hours. The deposit of thallium is washed with water, dried by pressing between filter paper, and fused under potassium cyanide. The metallic regulus is preserved in a sealed tube under a solution of thallium hydroxide. It does not contain any recognisable quantities of lead or arsenic. E. C. R.

Compounds of Hydrazine with Mercury Salts. By KARL A. HOFMANN and E. C. MARBURG (*Ber.*, 1897, **30**, 2019—2022).—The authors have prepared several hydrazine derivatives of mercury salts which are, in their opinion, analogous to the well-known mercuriammonium compounds. When mercuric chloride and hydrazine hydrate are brought together in solution in alcohol and ether, a compound of the formula $N_2H_4HgCl_2$ is precipitated; it is moderately stable when dry, but unstable when moist, and decomposes rapidly when heated, but does not explode. When this compound is shaken with water, or when sodium acetate is added to the mixed aqueous solutions of hydrazine sulphate and mercuric chloride, an unstable yellow compound, $N_2H_2Hg_2Cl_2$, is produced which explodes when heated or struck, and rapidly decomposes when moist, nitrogen being evolved and mercury and calomel left. It is readily soluble in hydrochloric acid, but always leaves a small residue of calomel. Alkalis decompose it rapidly. These two compounds appear to be strictly analogous to the fusible and infusible white precipitates, $2NH_3,HgCl_2$ and NH_2HgCl.

Somewhat similar compounds have also been obtained from mercuric nitrate. The substance $N_2H_4Hg(NO_3)_2$ is formed as a curdy precipitate when hydrazine nitrate and mercuric nitrate are mixed in aqueous solution; it is not explosive, dissolves in acids, and is decomposed by alkalis with evolution of nitrogen. When hydrazine nitrate reacts with mercurous nitrate in aqueous solution, an amorphous, white precipitate is produced, which consists of the compound $N_2H_4Hg_2(NO_3)_2$; in pure water, it rapidly decomposes with separation of mercury, and it does not explode when heated. This is the only known ammoniacal derivative of a mercurous salt, the others which have been described having been proved to be mixtures of mercury with the corresponding mercuric derivative. A. H.

Condition in which Elements other than Carbon exist in Iron and Steel. By ADOLPHE CARNOT and GOUTAL (*Compt. rend.*, 1897, **125**, 148—152, and 213—216).—When iron is dissolved in dilute hydrochloric acid out of contact with air, the greater part of the silicon is left undissolved in the form of an iron silicide, FeSi. The remainder of the silicon is converted into the hydroxide, $SiO(OH)_2$, and seems to exist in the iron in the form of silicides intermediate between Fe_3Si_2 and Fe_5Si_2. When the iron contains manganese, practically the whole of the latter is found in combination with the silicon in the insoluble residue, and it would seem to follow that silicon combines with manganese in preference to combining with iron.

When iron and steel are heated with dilute acids, almost all the sulphur is converted into hydrogen sulphide, but when the solvent is a neutral or faintly acid solution of cupric potassium chloride, all the sulphur remains in the insoluble residue, partly as iron sulphide, but often mainly as cupric sulphide. Direct experiment shows that the copper solution has no action on ferrous sulphide, and it follows that the suphur is partly present in the metal in the form of some other sulphide. Direct experiment shows that the sulphur in combination with copper in the residue is equivalent to the manganese present in the iron or steel, and hence it would seem that part of the sulphur exists in the iron or steel in the form of manganese sulphide, MnS, and that, at high temperatures, sulphur combines with manganese in preference to iron, a conclusion which agrees with the known use of spiegeleisen or ferromanganese for eliminating sulphur from cast-iron.

When the solvent is neutral cupric potassium chloride solution, all the phosphorus is found in the residue in the form of iron phosphide, Fe_3P, identical with that described by Schneider; arsenic, on the other hand, is completely dissolved by the copper solution, but if the solvent is dilute hydrochloric acid, and air is excluded, all the arsenic remains as such in the residue, and presumably exists uncombined in the metal, mixed with or dissolved in the iron.

Manganese, when in small quantity, is present in the form of silicide or sulphide, but when in larger quantity, part of it is either dissolved in or is combined with the iron, and the method of examination adopted is unable to determine the exact condition.

Copper is found as such in the residue left when the iron or steel is dissolved in dilute acids out of contact with air. Titanium behaves similarly with either solvent. It follows that copper and titanium both exist as such in the iron or steel.

Nickel is partially attacked by dilute acids, even out of contact with air, but the nickel left in the residue is in the metallic state, and is free from iron. Probably, therefore, it is simply mixed with or dissolved in the iron.

Chrome-steels are readily attacked by acids if they are highly carburetted, but not otherwise, and the composition of the residues indicates that the chromium is present in the form of chromium-iron carbides.

Tungsten is left undissolved by dilute acids, in the form of the compound Fe_3W, and molybdenum is left in the form of the compound Fe_3Mo_2. Both these compounds, therefore, exist in the iron or steel.

C. H. B.

Chromium. By HENRI MOISSAN (*Ann. Chim. Phys.*, 1896, [vii], 8, 559—570).—The preparation of pure chromium is fully described and its chief properties given (Abstr., 1893, ii, 281; 1894, ii, 452).

A. C. C.

Arsenothiomolybdates. By RUDOLPH F. WEINLAND and KARL SOMMER (*Zeit. anorg. Chem.*, 1897, **15**, 42—65).—*Sodium pyrothioarsenothiomolybdate*, $As_2S_7(MoS_3)_2Na_4 + 14H_2O$, is obtained by adding molybdenum trisulphide (2 mols.) to a solution of sodium thioarsenate (1 mol.) heated on the water bath; a portion of the trisulphide remains undissolved, and a brown bye-product is also formed. The filtrate, on evaporation, yields the salt mixed with the brown, amorphous bye-product, which, although insoluble in water, is easily soluble in a solution of the salt; the two are most conveniently separated by dissolving the crude salt in a large quantity of ice-cold water, when the brown bye-product remains for the most part undissolved. The salt is also formed on boiling a solution of sodium pyrothioarsenate with molybdenum trisulphide, but large quantities of bye-products are formed at the same time. It can, however, be easily obtained in a pure state by adding salicylic acid (1 mol.) to a solution of molybdenum trisulphide (1 mol.) in sodium thioarsenate (1 mol.), and precipitating the clear filtrate with alcohol. It crystallises in lustrous, dark red, six-sided prisms, gradually decomposes when dry, and is then no longer entirely soluble in water, is not hygroscopic, and loses its water of crystallisation at 105°. It is decomposed by dilute mineral acids with evolution of hydrogen sulphide and precipitation of a reddish-brown sulphide, and gives characteristic coloured precipitates with solutions of metallic salts. This salt is also produced by the action of arsenic pentasulphide on sodium thiomolybdate. The *potassium* salt, with $8H_2O$, which can be prepared in a similar manner to the sodium salt, crystallises in bright red, slender needles, is easily soluble in water, insoluble in alcohol, and has properties like those of the sodium salt. The *ammonium* salt, with $5H_2O$, is best prepared by adding salicylic acid (4 mols.) to a concentrated solution of ammonium pyrothioarsenate and ammonium thiomolybdate, and then precipitating with alcohol; it crystallises in slender, scarlet needles, is very unstable, and cannot be obtained pure. The aqueous solution quickly decomposes with evolution of ammonia and hydrogen sulphide. The *barium* salt, with $14H_2O$, is obtained by dissolving arsenic pentasulphide in a solution of barium thiomolybdate, and cooling the filtrate to −15°. It cannot be obtained by the action of molybdenum trisulphide on barium thioarsenate, as under these conditions sulphur is precipitated, and a double salt of barium thioarsenate and barium thioarsenite is formed. It crystallises in slender, red needles, and when recrystallised partially decomposes with separation of sulphur.

Sodium metathioarsenothiomolybdate, $AsS_3(MoS_3)Na + 6H_2O$, is obtained by treating the above sodium pyrothioarsenothiomolybdate with salicylic acid ($1\frac{1}{2}$ mol.) and a small quantity of water at 40—50°. The clear solution is precipitated with alcohol, and the precipitate washed with dilute alcohol and then with sufficient cold water to extract the

sodium salicylate and undecomposed pyrosalt. It is an amorphous, cherry-red powder, insoluble in water, and easily soluble in dilute sodium hydroxide and ammonia. The *potassium* salt, with $4H_2O$, obtained in a similar manner to the sodium salt, is an amorphous, red powder.

Potassium pyrothioarseno-oxythiomolybdate, $As_2S_7(Mo_2S_3O_3)K_4 + 6H_2O$, is obtained by boiling arsenic pentasulphide (1 mol.) with a solution of molybdenum trisulphide (2 mols.) in potassium hydroxide (4 mols.). On concentrating the solution, potassium pyrothioarsenothiomolybdate first crystallises out, and on further concentrating the mother liquors the salt separates in slender needles; it is also formed by the action of arsenic pentasulphide on a solution of molybdic acid in potassium hydrogen sulphide. It crystallises in yellow, slender, six-sided needles, is very easily soluble in water, and when the solution is treated with acetic acid it gradually becomes dark red; this reaction is characteristic of the oxythiomolybdates. With hydrochloric acid, it gives a yellowish-brown precipitate, also characteristic precipitates with solutions of the salts of the heavy metals. The salt with $10H_2O$, obtained by boiling a solution of potassium thiomolybdate with dipotassium arsenate, crystallises in yellow needles. The *sodium* salt, with $15H_2O$, is obtained by boiling ammonium thiomolybdate (2 mols.) with sodium hydroxide (4 mols.) until all the ammonium sulphide is driven off, and then adding arsenic pentasulphide, and boiling until the latter is dissolved. Metathioarseno-oxythiomolybdate, which is also formed during the reaction, crystallises out first, and the salt is obtained on concentrating the mother liquors. It crystallises in slender, yellow needles, and resembles the potassium salt. The *magnesium* salt, with $16H_2O$, prepared in a similar manner to the sodium salt, crystallises in slender, yellow needles, and the *barium* salt, with $12H_2O$, in slender, yellow needles.

Potassium metathioarseno-oxythiomolybdate, $AsS_3(MoO_2S)K + 2\frac{1}{2}H_2O$, obtained as a bye-product in the preparation of the preceding potassium salt from arsenic pentasulphide, molybdic acid, and potassium hydrogen sulphide, is a fine, orange-red powder, which partially decomposes when recrystallised; when treated with hydrochloric acid, all the arsenic and molybdenum are precipitated as a reddish-yellow powder, but the colour of the solution is not altered by acetic acid. With ammonium, barium, strontium, and calcium salts, it gives yellow, amorphous precipitates which are insoluble in cold water, and with salts of the heavy metals, it yields characteristic precipitates. When heated in a tube, sulphurous anhydride is given off; this decomposition takes place slowly at 100°, so that the determination of the water of crystallisation must be effected at 90°. The *sodium* salt, with $5H_2O$, is lemon-yellow when freshly prepared, and becomes reddish-yellow on recrystallisation; it resembles the potassium salt.

E. C. R.

Hydroxylamine-ammonia Compounds of Uranic Acid. By KARL A. HOFMANN (*Zeit. anorg. Chem.*, 1897, **15**, 75—80).—*Hydroxylamine ammoniouranate*, $UO_4(NH_3OH)_2,2NH_3$, is obtained by adding ammonia (7 per cent. 100 c.c.) to an aqueous solution of uranyl

nitrate (20 grams) and hydroxylamine hydrochloride (10 grams). The product, after being washed with dilute ammonia, alcohol, and ether, and dried at the ordinary temperature, is a lustrous, canary-yellow, crystalline powder consisting of microscopic, rhombic tablets; it is stable at the ordinary temperature, loses ammonia when heated at 73°, and decomposes with a slight explosion when heated to 178—180° in a capillary tube. It reduces Fehling's solution at the ordinary temperature, and when cautiously heated to 120° is converted into uranic acid, UO_4H_2.

Hydroxylamine uranate, $UO_4(NH_4O)_2 + H_2O$, can be obtained by heating the preceding compound with glycerol at 100°, by allowing it to remain with water at the ordinary temperature for some hours, or by treating it with hot water; it is also obtained when uranic acid or uranyl nitrate is digested with excess of an aqueous solution of hydroxylamine. It crystallises in yellow, elongated plates pointed at both ends at an angle of 126°. When heated, it decomposes with a slight explosion, yielding a greenish-black powder. It reduces Fehling solution with great ease.

Hydroxylamine ammonio-uranate, when treated with 2 mols. of acetic acid, yields ammonium acetate and hydroxylamine uranate; with excess of acetic acid, it yields a double salt of uranyl acetate and hydroxylamine acetate which crystallises in yellow, lustrous prisms.

E. C. R.

Zirconium Tetriodide. By LOUIS M. DENNIS and A. E. SPENCER (*J. Amer. Chem. Soc.*, 1896, **18**, 673—679).—Attempts to obtain this compound by passing iodine vapour over zirconium heated to dull redness in a current of hydrogen met with no success. It was, however, eventually obtained by passing hydrogen iodide, prepared by Merz and Holzmann's method (Abstr., 1889, 754) over zirconium. As the tube containing the latter was gradually heated, an amorphous, white sublimate, probably of ferrous iodide obtained from traces of iron in the metal, first formed, and finally, at a bright red heat, a white, crystalline sublimate was deposited immediately beyond the red hot portion of the tube. After cooling in a current of hydrogen, the zirconium was found to have changed from black to greyish-white, but contained very little iodine. The composition of the crystalline sublimate, which consists of colourless cubes exhibiting no double refraction, proved on analysis to correspond with the formula ZrI_4. It is insoluble in water, nitric acid, hydrochloric acid, aqua regia, and carbon bisulphide, but decomposed and dissolved by concentrated sulphuric acid and partially decomposed by concentrated nitric acid with liberation of iodine and formation of a white powder insoluble in nitric acid but soluble in concentrated sulphuric acid. On heating in hydrogen, the iodide turns black, and iodine and hydriodic acid are formed, and on heating in the air it melts and sublimes. The iodide is unchanged by boiling with water, in this respect resembling Deville's fluoride, but differing from the deliquescent, easily decomposable tetrachloride and tetrabromide.

E. W. W.

Double Fluorides of Zirconium with Lithium, Sodium, and Thallium. By HORACE L. WELLS and H. W. FOOTE (*Amer. J. Sci.*,

1897, **3**, 466—471).—Thallium fluoride was prepared by dissolving the metal in sulphuric acid, adding an excess of baryta water, filtering, and passing carbonic anhydride into the hot solution; the filtrate was then evaporated and treated with excess of hydrofluoric acid. The salts were prepared by mixing the acid fluorides in varying proportions, evaporating and cooling to crystallisation. In all cases they are stable in the air.

The *salt* $2LiF,ZrF_4$, formed when 0·7—2 grams of lithium fluoride is added to 20 grams of zirconium fluoride, crystallises in hexagonal prisms very similar to the crystals of quartz found in Herkimer Co., N.Y.; when recrystallised, it is converted into the 4 : 1 salt. The *salt* $4LiF,ZrF_4 + \frac{2}{3}H_2O$, obtained when 5—7 grams of lithium fluoride is added to 20 grams of zirconium fluoride, is somewhat difficult to prepare owing to the insolubility of lithium fluoride; it separates in crystalline crusts. On recrystallising, lithium fluoride is precipitated.

The *salt* $2NaF,ZrF_4$ is prepared by adding 2 parts of sodium fluoride to 14 parts of zirconium fluoride; it separates in crusts of minute, hexagonal crystals and cannot be recrystallised. The *salt* $5NaF,2ZrF_4$, previously described by Marignac, is formed under very wide conditions; it crystallises in thick, orthorhombic prisms.

The *salts* TlF,ZrF_4 and $TlF,ZrF_4 + H_2O$ are obtained when 1 part of thallium fluoride is mixed with 3—4 parts of zirconium fluoride; the hydrated salt crystallises in needles if the solution is cooled before precipitation occurs, but if the solution is evaporated until crystals begin to form and is then cooled, the anhydrous salt separates in minute, square plates. When recrystallised, it is converted into the 5 : 3 salt. The *salt* $5TlF,3ZrF_4$, is prepared by mixing 1—3·5 parts of thallium fluoride with 1 part of zirconium fluoride; it crystallises in needles. When, however, 4 parts of thallium fluoride are employed, the same salt is produced, but it crystallises in hexagonal prisms. Both modifications, when recrystallised, separate in needles. The *salt* $3TlF,ZrF_4$ is obtained when 1 part of zirconium fluoride is added to 4—20 parts of thallium fluoride; it crystallises in brilliant octahedra and can easily be recrystallised. E. C. R.

Mineralogical Chemistry.

Argentiferous Gold from Lower California. By CARLOS F. DE LANDERO (*Mem. Soc. Cient. "Antonio Alzate," Mexico*, 1896, **10**, 75—77).—Rounded grains of gold of a pale yellow colour, from the placers at Alamo, district Norte del Territorio, Lower California, gave on analysis,

Au.	Ag.	Quartz sand.	Total.
80·58	17·22	1·39	99·19.

This corresponds with Au_5Ag_2. Specimens of electrum from Colombia and the Urals have nearly the same composition.

L. J. S.

Arsenic Compounds of Iron, Nickel and Cobalt. By CARL FRIEDRICH RAMMELSBERG (*Jahrb. f. Min.*, 1897, ii, 45—66).—Löllingite, mispickel, niccolite, rammelsbergite, smaltite, chloanthite, gersdorffite, cobaltite, skutterudite &c., the cubic, orthorhombic and rhombohedral arsenides and antimonides of iron, nickel and cobalt, may all be represented by the general formulæ $RS_2,xR_m(As,Sb)_n$. Here $m:n$ varies from 1 : 1 (in niccolite) to 1 : 3 (in skutterudite), and between these limits there can be variations without alteration of crystal form; the various ratios of $R_m:As_n$ must therefore be considered as forming isomorphous mixtures. Similar cases of variation of composition without effect on the crystal form is shown by artificial alloys containing arsenic or antimony, and in the mineral dyscrasite. The sulphur of the isomorphous portion RS_2, gradually increases in amount from zero until $x = 1$.

Numerous analyses of these minerals are discussed in detail, and special formulæ given to suit the various cases. For löllingite are given, Fe_3As_4 (leucopyrite), $FeS_2,4Fe_2S_3$; $2FeS_2,3Fe_5As_8$; $3FeS_2,Fe_3As_5$, &c. Mispickel, which is generally $FeS_2,FeAs_2$, is also represented by $5FeS_2,Fe_6As_{11}$; $8FeS_2,7FeAs_2$, &c., in order to explain the variations shown by the sulphur. In the nickel and cobalt compounds, the ratios taken for $m:n$ are, 1 : 1, 1 : 1·33, 1 : 1·5, 1 : 1·66, 1 : 2, 1 : 2·5, and 1 : 3; whilst x varies considerably, for example, in passing from smaltite to cobaltite. L. J. S.

Composition of Nagyagite. By EDUARD PŘIWOZNIK (*Chem. Centr.*, 1897, ii, 54; from *Österr. Zeit. Berg-Hütt.*, 1897, 45, 265—267).—The composition of nagyagite is doubtful; the present analysis leads to the formula $Te_6Pb_6AuS_8 = 4PbS,2PbTe,AuTe_2 + 2TeS_2$.

Te.	S.	Au.	Pb.	Total.
29·88	10·73	8·11	51·18	100·00.

L. J. S.

Formation of Cuprite by Electrolysis of Copper Sulphate Solution. By QUIRINO MAJORANA (*Rend. Accad. Linc.*, 1895, 4, i, 371—375).—Small crystals of cuprite are formed on electrolysing a saturated neutral solution of copper sulphate at the ordinary temperature, using a very small current density; as the solution becomes acid by continued electrolysis, crystals of metallic copper make their appearance, and if the solution is acid to start with, no cuprite crystals are formed. The author finds also that the quantity of free acid necessary to prevent the formation of cuprite crystals is less in proportion as the current density is greater. W. J. P.

Formation of Bauxite and allied Minerals. By A. LIEBRICH (*Zeits. prakt. Geol.*, 1897, 212—214. Compare this vol., ii, 104).—Alumina is not liberated from silicates by the ordinary weathering agencies; it is therefore, in its various combinations (hydrates, sulphates, aluminates), of much less common occurrence than the easily liberated oxides of iron. The action of sulphuric acid, derived from pyrites or hydrogen sulphide, on aluminium silicates would give rise to solutions of aluminium sulphate, from which the various mineral sulphates or hydrates (bauxite, &c.) could be deposited. Sulphuric

acid in contact with fluorides gives hydrogen fluoride, which, in acting on aluminium silicates, would give aluminium fluorides (cryolite, &c.). It is suggested that aluminates (spinel, MgO,Al_2O_3, for example) may have been formed by the loss of sulphuric acid and water from the corresponding double sulphates; for example, pickeringite,

$MgO,Al_2O_3,(SO_3)_4 + 22H_2O$. L. J. S.

Fluorite from Argentina. By JEAN VALENTIN (*Zeit. prakt. Geol.*, 1896, 104—107).—Coarsely crystalline fluorite occurs in veins at the granite-gneiss contact, 20 kilometres south of San Roque, prov. Cordoba. It is accompanied by quartz and a little pyrites. Several analyses are given, the amount of calcium fluoride varying from 84·20 to 98·12 per cent.; the purest gave

	CaF_2.	$Al_2O_3 + Fe_2O_3$.	MgO.	SiO_2.
Dark blue, almost black ...	96·59	1·20	trace	2·08
Greenish	97·03	2·52	,,	trace
Greenish-white	98·12	1·68	,,	,,

Blue or violet fluorite occurs with galena, cassiterite, &c., in the wolframite and molybdenite veins of the Sierra de Cordoba. Previously this mineral had only been known to occur in Argentina in small amount. L. J. S.

Occurrence of Iodine in Malachite. By WILHELM AUTENRIETH (*Zeit. physiol. Chem.*, 1897, **22**, 508—513).—Examination of a specimen of malachite, of unknown locality, showed that it contained both iodine and chlorine, the amount of halogen varying, in the case of iodine, from 0·08—0·4 per cent., and in that of chlorine from 1·8—5·5 per cent. The same mineral also contained traces of iron, calcium, magnesium, and several per cent. of a residue insoluble in hydrochloric acid. The author has further examined a large number of malachites from known localities, also atacamite and azurite, without, in any single instance, being able to detect even traces of iodine. In all probability, the mineral examined was a specimen of Chilian atlasite, which is known to contain as much as 8 per cent. of copper chloride. A. W. C.

Formula of Apatite. By CARL F. RAMMELSBERG (*Jahrb. f. Min.*, 1897, ii, 38—44).—The ratio $(F + Cl) : P = 1 : 3$, required by the well-known apatite formula $3Ca_3P_2O_8 + Ca(F,Cl)_2$ ("normal apatite"), although supported by several later analyses, does not always hold good. In the latter case, the formula must be written as $3Ca_3P_2O_8 + Ca(F_2,O)$, since there is a slight excess of calcium over that required to combine with the phosphoric acid and fluorine. Several recent analyses by Carnot (Abstr., 1896, ii, 611) are of this kind; his analysis of apatite from Greiner, in the Zillerthal, with only 0·37 per cent. fluorine, corresponds with $3Ca_3P_2O_8 + Ca(O_{11/12},F_{2\,1/12})$. Völker's analysis (1858) of apatite from Kragerö, with 4·20 per cent. chlorine and no fluorine, corresponds with $3Ca_3P_2O_8 + Ca(O_{2/5},Cl_{2\,3/5})$; Laspeyres finds only a trace of fluorine in this apatite.

The question arises whether apatites which are poor in fluorine are of original formation, or have been derived by the alteration of normal apatite, fluorine having been abstracted, and a basic phosphate

formed. The latter is here considered to be the more probable, since CaO and CaF_2 are not isomorphous, and, further, apatite is easily altered by the action of waters into phosphorite, pseudoapatite, &c. This view is supported by the fact that many of Carnot's analyses show the presence of impurities. L. J. S.

A Basic Sulphate of Copper. By GIUSEPPPE CESÀRO and H. BUTTGENBACH (*Ann. Soc. Geol. Belgique*, 1897, **24**, *Bull.*, pp. xli—xliii). —The specimen described, which is probably from Nassau, is a compact green mass of small crystals. Microscopical examination shows the crystals to be orthorhombic and apparently hemimorphic; they are flattened parallel to the perfect pinacoidal cleavage. The acute positive bisectrix is parallel to this cleavage. Analyses lead to the formula $CuSO_4,2Cu(OH)_2$. This, which seems to be a new mineral, differs from brochantite, $CuSO_4,3Cu(OH)_2$, in its optical characters. Friedel has prepared a basic copper sulphate having the composition $CuSO_4,2Cu(OH)_2$. L. J. S.

Constitution and Classification of Sulpharsenites, &c. By VASILE C. BUTUREANU (*Bul. Soc. Sci. Bucarest*, 1897, **6**, 172—182).— Several of the hypothetical thio-acids of the general formula $m(AsS_3H_3) - nSH_2$ are expressed graphically, and the corresponding structural formulæ are given for all the known mineral sulpharsenites, sulphantimonites and sulphobismuthites. Stephanite, polybasite, and polyargyrite cannot be written graphically as basic salts of the ortho-acid (SbS_3H_3), they are accordingly supposed to be tetrabasic diortho-sulphantimonites $(Sb_2S_5Ag_4)$ with an excess of silver sulphide. L. J. S.

Analyses of Serpentines. By GINO TURI (*Gazzetta*, 1897, **27**, ii, 82—86).—The author has analysed serpentines from the locality dell' Impruneta near Florence; the serpentine is of two kinds, white and green, and was separated before analysis. The accompanying table gives the analytical results; A and B refer to samples from the Black Rock Hill (Poggio dei Sassi Neri) and C and D are from the Mine dell' Impruneta (Miniera dell' Impruneta).

	A.		B.		C.		D.	
	White.	Green.	White.	Green.	White.	Green.	White.	Green.
H_2O	13·40	12·65	13·70	12·80	13·02	12·06	12·85	11·70
SiO_2	42·00	39·55	42·80	43·87	41·04	42·56	40·92	42·12
FeO	2·30	6·49	3·42	2·45	1·53	3·02	2·45	4·80
Fe_2O_3	5·75	7·86	5·09	10·75	4·60	8·34	4·32	7·05
MgO	36·40	32·53	33.94	29·36	39·03	33·60	39·05	33·15
Cr_2O_3	0·00	0·00	0·00	0·00	0·00	0·20	0·00	0·28
Total	99·85	99·08	98·95	99·23	99·22	99·78	99·59	99·10

The serpentines also contain traces of calcium and sodium.
W. J. P.

Rœblingite, a New Silicate from Franklin Furnace. By SAMUEL L. PENFIELD and H. W. FOOTE (*Amer. J. Sci.*, 1897, [iv], 3, 413—415; and *Zeits. Kryst. Min.*, 1897, **28**, 578).—Rœblingite occurs as dense, white, compact masses filling cavities in axinite which forms veins in the garnet rock of the zinc deposits of Franklin, New Jersey. Under the microscope, it is seen to consist of an aggregate of minute, prismatic crystals with parallel extinction and weak double refraction. The hardness is a little below 3; sp. gr. 3·433. The powdered mineral is easily soluble in dilute acids, with separation of gelatinous silica and evolution of sulphurous anhydride. The mean of two very similar analyses by Foote is

SiO_2.	SO_2.	PbO.	MnO.	CaO.	SrO.	K_2O.	Na_2O.	H_2O.	Total.
23·58	9·00	31·03	2·48	25·95	1·40	0·13	0·40	6·35	100·32

This gives the molecular ratios as $SiO_2 : SO_2 : PbO : (Ca, Mn, Na_2, \&c.\ O) : H_2O = 5{\cdot}61 : 2{\cdot}01 : 1{\cdot}99 : 7{\cdot}43 : 5{\cdot}04$, from which the formula is given doubtfully as $H_{10}Ca_7Pb_2Si_5S_2O_{28} = 5H_2CaSiO_4 + 2(CaO,PbSO_3)$. As the water can only be driven off at a rather high temperature, it is to be regarded as hydroxyl. It is not probable that the mineral is a mixture or contains much foreign material, and is the first naturally occurring sulphite that has been observed. The name is given after W. A. Rœbling.

L. J. S.

Monoclinic Pyroxenes of New York State. By HEINRICH RIES (*Jahrb.f. Min.*, 1897, ii, Ref. 26—28; from *Ann. N.Y. Acad. Sci.*, 1896, **9**, 126—178).—In this monograph, detailed descriptions are given of all the known occurrences of monoclinic pyroxenes (except wollastonite) in the State of New York. They occur in gneisses and gabbros, in contact- and dynamo-metamorphic limestones, and in magnetite. The lighter coloured varieties are found in the dynamo-metamorphic limestones, and the darker in the contact-limestones; those from the magnetite are almost opaque in thin sections. On the crystals, 16 forms are noted; the habit of each occurrence is very characteristic. Tschermak's assertion that Ca is always greater than Mg + Fe, does not hold good for these aluminous pyroxenes. The darker pyroxenes are usually altered to uralite, and the lighter to tremolite, other decomposition products being serpentine, chlorite, rose-red garnet, and clintonite. The following analyses are given.

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	Alkalis.	Loss on ignition.	Total.	sp. gr.
I.	54·63	5·26	—	3·00	22·63	14·18	—	—	99·70	—
II.	53·97	4·94	0·50	8·63	23·96	7·32	—	—	99·32	3·36
III.	56·00	8·44	4·70	2·40	21·63	5·23	0·50	0·20	99·10	3·5
IV.	56·14	8·19	0·38	2·85	17·79	13·67	—	—	99·02	—
V.	46·28	7·38	2·21	14·80	18·78	8·91	—	1·115	100·065	3·386
VI.	54·57	3·09	—	1·30	21·42	18·56	0·40	0·15	99·49	—
VII.	49·12	7·49	3·53	15·98	17·30	6·06	—	—	99.48	3·60
VIII.	52·01	5·82	0·67	6·86	26·90	11·26	0·50	—	104·02	3·60
IX.	50·05	7·16	0·56	—	25·63	14·48	—	1·66	99·54	3·26
X.	53·30	4·11	—	0·80	24·82	16·18	—	0·15	99·36	3·18
XI.	54·86	0·75	—	1·30	24·13	18·14	0·35	0·10	99·63	3·29
XII.	54·57	1·12	—	1·80	23·25	17·78	0·70	0·38	99·60	3·27
XIII.	54·94	2·42	—	1·29	25·38	17·60	0·28	—	101·91	3·00

The following optical determinations (extinction angle $\acute{c} : \mathfrak{c}$, &c.), show no definite relation to the amount of ferrous oxide present.

	$\hat{c}:\mathfrak{c}$	2V	α	β	γ	$FeO + Fe_2O_3 + Al_2O_3$
II.	41° 30′	60° 40′	1·6888	1·6932	1·7108	14·07
VI.	41 30	59 40	1·6806	1·6843	1·7036(Na)	4·39
X.	40	59	1·6778	1·6848	1·7025 ,,	4·91
XI.	40	59 30 (Na)	1·6749	1·6852	1·7013 ,,	2·05
XII.	41	56 30 ,,	1·6683	1·6730	1·6902 ,,	2·92
XIII.	37	58 56 ,,	1·6626	1·6718	1·6940 ,,	3·71

Other optical determinations are also compared with the amount of $FeO + Fe_2O_3 + Al_2O_3$.

I. Granular, transparent, light grey, in calcite. Cascadeville, Essex Co.

II. Dark green crystals in contact limestone. Diana, Lewis Co.

III. Black crystals in calcite. Weston Magnetite mine, Keene, Essex Co.

IV. Dark green prismatic grains in limestone. Keene, Essex Co.

V. Diallage in gabbro. Mt. Marcy, Essex Co.

VI. Green crystals with microcline and albite. Pitcairn, St. Lawrence Co.

VII. Black, with magnetite. Port Henry, Essex Co.

VIII. Dark green crystals in scapolite in contact limestone. Warwick, Orange Co.

IX. Leucite-augite in grains with calcite and seybertite. Amity, Orange Co.

X. Light, transparent crystals in limestone. Sing-Sing, Westchester Co.

XI. Diopside. De Kalb, St. Lawrence Co.

XII. White, in limestone. Port Henry, Essex Co.

XIII. Green, glassy diopside. Russell, St. Lawrence Co.

L. J. S.

Chabazite with Crystal-water Crystal-carbon-bisulphide, &c. By FRIEDRICH RINNE (*Jahrb. f. Min.*, 1897, ii, 28—37).—The fact, recently discovered by G. Friedel (Abstr., 1896, ii, 481), that dehydrated zeolites absorb ammonia and other gases, may be due to a mechanical condensation of the gas or to molecular action; in the latter case, there would be a corresponding change in the physical characters of the zeolite. In order to test this, the present author has made optical examinations of chabazite. A partially dehydrated crystal plate of the mineral when placed in liquid carbon bisulphide exhibits a gradual change in the extinction angles, and becomes more strongly birefringent; on heating the plate, the carbon bisulphide is expelled with a return to the original optical characters. The absorption of carbonic anhydride, alcohol, chloroform, benzene, or aniline is also accompanied by similar changes in the optical characters.

L. J. S.

Meerschaum. BY R. HELMHACKER (*Berg. u. huettenm. Zeit.*, 1897, **61**, 44—46).—By surface agencies, serpentine is altered into an impure limonite, or, when not actually exposed, into a clay-like, crumbly mass consisting of opal, quartz, magnesite, gymnite and talc; when the earth-covering is of considerable thickness, nodules of meerschaum are

also formed. The associated opal and magnesite occur intimately intermixed with the meerschaum, which explains the variations in composition shown by analyses. Freshly obtained meerschaum is soft and dough-like and of a pale green colour; it is only on exposure to the air that it becomes hard and white. The occurrences of meerschaum in Moravia, Bosnia, and Asia Minor are described. The associated magnesite from Hrubšic, in Moravia, gave on analysis.

CO_2.	MgO.	CaO.	Al_2O_3,Fe_2O_3.	SiO_2.	P_2O_5.	Total.
51·60	46·10	1·45	0·81	0·60	0·24	100·80

L. J. S.

Wellsite, a New Mineral. By JULIUS H. PRATT and H. W. FOOTE (*Amer. Journ. Sci.*, 1897, [iv], **3**, 443—448; and *Zeits. Kryst. Min.*, 1897, **28**, 581).—This new zeolite occurs with albite, hornblende and chabazite in a corundum vein at Buck Creek corundum mine, Clay Co., North Carolina. The small, isolated crystals are invariably interpenetration twins closely resembling those of phillipsite and harmotome, the twin planes being, as in these species, $c(001)$ and $e(011)$. The monosymmetric constants are given below. The crystals are colourless and transparent to white, with a vitreous lustre; they are brittle and possess no cleavage. H = 4—4·5; sp. gr. = 2·278—2·366. The acute, positive bisectrix is perpendicular to (010), and the optic axial angle is large. The mineral is decomposed by hot hydrochloric acid with separation of silica, but without gelatinisation. The mean of two analyses is,

SiO_2.	Al_2O_3.	BaO.	SrO.	CaO.	MgO.	K_2O.	Na_2O.	H_2O.	Total.
43·86	24·96	5·07	1·15	5·80	0·62	3·40	1·80	13·35	100·01.

This gives the formula $R''Al_2Si_3O_{10} + 3H_2O$, in which, approximately, $BaO : CaO : (K,Na)_2O = 1 : 3 : 2$. About one-third of the water is expelled between 100° and 200°, another third at 200—300°, and the remainder on ignition. After being heated to 265°, nearly all the water is regained from moist air. The close relation of the new mineral to the phillipsite group is shown by the following table.

		a	:	b	:	c	β
Wellsite,	$RAl_2Si_3O_{10} + 3H_2O$ ...	0·768	:	1	:	1·245	53 °27′
Phillipsite,	$RAl_2Si_4O_{12} + 4\frac{1}{2}H_2O$...	0·7095	:	1	:	1·2563	55 37
Harmotome,	$RAl_2Si_5O_{14} + 5H_2O$ ...	0·7032	:	1	:	1·2310	55 10
Stilbite,	$RAl_2Si_6O_{16} + 6H_2O$ ...	0·7623	:	1	:	1·1940	50 50

Here the ratios $RO : Al_2O_3$ and $SiO_2 : H_2O$ are constant, and = 1 : 1; phillipsite is, however, an exception to this, and it should therefore probably have only $4H_2O$. Another member of this series would be expected to be $RAl_2Si_2O_8 + 2H_2O$, this being related to the anorthite formula in the same way that stilbite is related to albite.

L. J. S.

[Orthoclase, Melanite and Zircon from Alnö.] By ARVID G. HÖGBOM (*Zeits. Kryst. Min.*, 1897, **28**, 506; from *Geol. För. i Stockholm Förh.*, 1895, **17**, 137, 145, 148).—In a paper on the geology and petrology of the nephelite-syenite district of the Island of Alnö, Sweden,

the following mineral analyses are given. Orthoclase, containing barium, I. Melanite, II; the Fe_2O_3 includes a little FeO. Zircon, III. (Analyses I and II are by N. Sahlbom; III by P. J. Holmquist).

	SiO_2.	ZrO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	Na_2O.	H_2O.	Total.
I.	62·10	—	—	19·46	—	trace	—	0·89	1·19	0·67	
II.	31·15	—	6·73	3·14	23·83	—	0·58	33·44	0·68	—	99·35
III.	29·68	64·94	trace	—	—	1·15	0·28	—	—	3·86	99·91

	BaO.	MgO.	K_2O.	Total.
I. cont.	1·45	1·08	12·85	99·69.

L. J. S.

[**Babingtonite, Biotite, Almandine, and Gedrite from Massachusetts.**] By BENJAMIN K. EMERSON (*Zeits. Kryst. Min.*, 1897, **28**, 502—504; from *Bull. U.S. Geol. Survey*, 1895, No. **126**, 1—180).—All the published information respecting the minerals found in Franklin, Hampshire, and Hampden counties, Massachusetts, is collected together in lexicon form, several new analyses, crystallographic and other observations, being also included. Babingtonite occurs as a black layer, sometimes showing crystal faces, coating fissures in the gneiss at Buckland; it gave analysis I, by E. A. Schneider, also a trace of boric acid. Biotite, from mica-schist at Goshen, gave II, by G. Steiger. Almandine crystals, from the schists at Goshen, enclose radially arranged bands of quartz grains; analysis III (Steiger). Gedrite forms a rock at Warwick; the brown crystals are optically negative and moderately pleochroic, and enclose rutile; analysis IV, (Schneider), also 0·05 P_2O_5.

	SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	MgO.	K_2O.	Na_2O.	H_2O.	Total.
I.	52·48	trace	1·91	23·24		0·37	19·31	1·55	—	—	1·44	100·00
II.	36·96	0·91	21·15	2·80	15·54	—	0·23	7·87	7·47	1·00	2·93	96·86
III.	37·30	0·24	21·84	0·98	32·62	1·86	3·19	2·50	—	—	—	100·53
IV.	47·86	0·63	14·09	0·33	13·41	0·14	0·57	19·89	0·06	0·93	2·46	100·42

Several analyses of serpentine by Steiger are also given.

L. J. S.

Garnet from Sardinia. By DOMENICO LOVISATO (*Jahrb. f. Min.*, 1897, ii, Ref., 32; from *Rend. R. Accad. Lincei*, 1896, **5**, i, 56—63).—In Sardinia, garnet occurs in Archæan rocks, in magnetite, in mineral veins, and in the younger volcanic rocks. At Caprera, it is abundant, with tourmaline, in a gneiss-like mica-schist; on the Punta rossa peninsula, these schists are cut by veins of a rose-red rock also containing much rose-red garnet in small crystals. Analysis by Fasolo gave:

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	MgO.	Total.
37·80	18·03	3·20	23·40	17·04	0·48	0·34	100·29.

It is therefore spessartite. Sp. gr. 4·1016. L. J. S.

Perlitic Pitchstone from New South Wales. By WILLIAM F. SMEETH (*Jahrb. f. Min.*, 1897, ii, Ref., 83—84; from *Journ. and Proc. Roy. Soc., N.S.W.*, 1895, **28**, (for 1894), 306—320).—Pitchstone from the Tweed River, N.S.W., gave on analysis,

SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	K_2O.	Na_2O.	H_2O.	Total.	Sp. gr.
75·51	14·30	1·01	1·81	0·24	2·89	1·21	2·84	99·81	2·47

Corresponding with

Quartz.	Sanidine.	Albite.	Hypersthene.	Glass.	Water.
5·11	14·94	2·07	1·90	73·14	2·84 = 100.

These minerals occur as phenocrysts in the glassy base. The presence of hypersthene in so acid a rock is remarkable; it encloses magnetite, zircon, and apatite. The glass contains K_2O, 0·78; Na_2O, 1·14 per cent.

The perlitic structure admirably shown by this rock is described in detail, and the so-called perlitic cracks in quartz are discussed (compare *Geol. Mag.*, 1896, **3**, 15). L. J. S.

Quartz-mica-diorite from Val Camonica. By CARLO RIVA (*Jahrb. f. Min.*, 1897, ii, Ref., 65—66; from *Atti. Soc. Ital. Sci. nat.*, 1896, **36**, 139—159).—A quartz-mica-diorite near Rino, in the Val Camonica, consists of oligoclase, brown mica, quartz and sphene; there is a little orthoclase, but no hornblende. Analysis gave the results under I; under II is the analysis of a similar rock from Val Moja in the Adamello Mountains.

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	K_2O.	Na_2O.	H_2O.	Total.
I.	65·73	16·20	2·66	1·68	3·12	1·28	1·89	4·12	1·47	98·15
II.	66·75	15·90	3·73	1·84	3·11	1·23	1·98	3·38	1·22	99·14

The surrounding phyllites, when unaltered, consist mainly of quartz with chlorite and a little felspar; near the diorite, they contain the following secondary minerals: biotite, andalusite, staurolite, cordierite, muscovite, tourmaline, and garnet. L. J. S.

Gabbros of Arolla. By A. BRUN (*Jahrb. f. Min.*, 1897, i, Ref., 474—475; from *Arch. Sci. phys. nat.*, 1894, **32**, 102—109).—The gneiss of the district of Mt. Collon and the Arolla Glacier, in the Pennine Alps, is cut by dykes of gabbro. This contains anorthite, labradorite, diallage, olivine, hypersthene, and hornblende, together with secondary actinolite, mica, &c. The following analyses of the rocks are by A. Brunet; in III there is also a trace of fluorine.

	SiO_2.	Fe_2O_3.	FeO.	Al_2O_3.	CaO.	MgO.	K_2O.	Na_2O.	FeS.	MnO.	H_2O	Total.
I.	48·40	—	4·28	17·53	11·11	16·51	1·8		0·52	—	0·76	100·91
II.	47·45	2·80	3·60	19·25	14·00	8·61	2·20	1·0	trace	trace	1·65	100·56
III.	41·55	11·38	1·35	21·40	7·80	12·20	0·24	0·80	0·50	,,	3·65	100·87
IV.	48·90	2·52	3·20	18·08	14·10	11·43	0·25	1·53	trace	,,	0·88	100·89
V.	47·00	2·31	3·20	23·67	11·40	8·72	0·7	2·4	—	,,	0·62	100·02

L. J. S.

Dyke Rocks from Alnö. By NAIMA SAHLBOM (*Jahrb. f. Min.*, 1897, ii, 97—101).—The following analyses are given of Dyke rocks from the nepheline-syenite district of the Island of Alnö, Sweden. I. Nephelinite from S. Berge, consisting of a ground-mass of nepheline, altered to natrolite, and ægirite needles, with phenocrysts of ægirite and ægirite-augite; from the analysis, the mineralogical composition is calculated as, ægirite and ægirite-augite 23·2, natrolite 63·1, nepheline 8·7 per cent. II, Monchiquite from S. Berge, consisting of a colourless ground-mass of nepheline (or analcite), with pyroxene needles and large, violet-grey augite prisms; calcite, sphene, apatite and pyrites are also present. III, Ijolite-porphyry from Ås, consisting of a fine-grained mass of nepheline, pyroxene, and melanite, with some

apatite and pyrites, and phenocrysts of melanite and pyroxene; the analysis corresponds with, melanite, 30·4; ægirite and ægirite-augite, 30·5; nepheline 35·0 per cent. IV, Alnöite from Norrwik (also 0·25 fluorine) consisting of a ground-mass of calcite with melilite and a little brown mica, also much magnetite and perofskite, and phenocrysts of apatite and olivine; this rock is nearer to the true melilite-basalts than to typical alnöite.

	SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.
I.	49·07	0·64	19·46	2·30	3·50	0·38	3·82
II.	42·57	2·50	15·90	2·10	6·85	0·79	10·55
III.	42·02	2·36	12·05	7·93	5·06	0·96	17·01
IV.	29·25	2·54	8·80	3·92	5·42	trace	17·86

	MgO.	K_2O.	Na_2O.	H_2O.	CO_2.	P_2O_5.	S.	Total.
I.	0·60	4·39	9·25	5·99	trace	trace	—	99·40
II.	3·18	3·88	4·71	2·00	4·87	,,	trace	99·90
III.	2·18	3·15	4·95	0·67	—	1·66	0·54	100·54
IV.	17·66	2·45	0·77	2·61	6·00	2·86	trace	100·29

L. J. S.

Green Earth from Monte Baldo. By C. WILHELM VON GÜMBEL (*Jahrb. f. Min.*, 1897, ii, Ref., 33—35; from *Sitz.-Ber. Akad. München*, 1896, **26**, 545—604).—Green earth occurring, mixed with hornstone, as veins in Tertiary basalt-tuff on Monte Baldo, in the Tyrol and quite near to the Italian frontier, gave analysis I—III, by A. Schwager. It is of a dark bluish-green colour; sp. gr. 2·850—2·920; hardness 1 and 3½. By long digestion with hydrochloric or sulphuric acid, the fine powder is completely decomposed, with separation of pulverulent silica. In thin sections, it has a cloudy appearance with aggregate polarisation.

	SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	MgO.	K_2O.
I.	54·80	0·22	7·38	13·12	7·09	0·18	0·20	3·18	8·48
II.	55·80	0·24	3·20	16·85	3·88	0·12	0·16	5·32	9·04
III.	54·84	0·10	1·22	19·16	4·39	0·28	0·24	5·34	9·75
IV.	50·36	0·02	7·04	19·13	3·95	0·06	0·91	4·08	6·62

	NaO.	Li_2O.	P_2O_5.	H_2O.	Organic matter	Total.
I.	0·62	—	0·10	4·99	trace	100·36
II.	1·12	—	0·07	4·67	,,	100·47
III.	0·82	—	—	3·77	,,	99·91
IV.	1·58	0·01	0·26	6·32		100·34

Glauconite in reniform masses from Monte Brione, on Lago di Garda, gave IV, by Schwager. It closely resembles the green earth in appearance; the colour is dark grey to black, and the streak dirty blue-green. Sp. gr. 2·955 and 2·952; hardness 3. The glauconite is more easily decomposed by hydrochloric acid than the green earth; 2 per cent. acid dissolves, in 8 hours, 58·08 per cent. of the former, and 23·86 of the latter, the soluble portion in both cases having the same composition as glauconite. Caustic potash partially dissolves both minerals.

From the behaviour with acid, it is concluded that the Monte Brione glauconite is a simple mineral, although the analysis does not lead to

a definite formula. The green earth may, however, be a mixture. These minerals, which have many characters in common, are placed in the mica group; and for the green earth of volcanic rocks the name celadonite (seladonit) is retained, whilst that of sedimentary rocks is called glauconite. Near the Tyrolese-Italian border, these green earths are worked commercially for paints. L. J. S.

Water of the Adler Spring at Wiesbaden. By C. Remigius Fresenius and Heinrich Fresenius (*Jahrb. nassau. Ver. Naturk.*, 1897, **50**, 3—21).—The water of the Adler spring at Wiesbaden is slightly yellowish, and on standing gives an ochreous deposit; it has a temperature of 64·4°. Sp. gr. 1·00626 at 19°. In 1000 parts are: Na_2O, 3·626856; K_2O, 0·108983; Li_2O, 0·009217; NH_4, 0·004778; CaO, 0·499457; BaO, 0·000287; SrO, 0·013545; MgO, 0·078575; FeO, 0·004025; MnO, 0·000758; Cl, 4·666173; Br, 0·003818; I, 0·000032; SO_3, 0·056197; P_2O_5, 0·000030; As_2O_5, 0·000119; B_2O_3, 0·000986; SiO_2, 0·062262; total CO_2, 0·593732. Total solids 8·342868; free CO_2, 0·142038. Rubidium, cæsium, copper, titanic acid, nitric acid, hydrogen sulphide and organic matter are also present in minute traces. The composition of this water is like that of all the other warm salt springs of Wiesbaden (this vol., ii, 109); it is compared with that of the Kochbrunnen. L. J. S.

Mineral Waters in Canton Graubünden. By Gustav Nussberger (*Jahresber. Naturf. Ges. Graubünden's*, 1896, **39**, 67—76).—Mineral waters, rich in calcium sulphate, from springs in the Canton Graubünden (Grisons), Switzerland, gave the following results on analysis, in parts per 10,000. I, Springs at Juf. II, Sassal spring; temperature, 8·1°; sp. gr. 1·0011; also MnO, 0·0100. III, Peiden springs in the Lugnetz-thal; temperature 12·2°; sp. gr. 1·00365. IV, Spring in the Val d'Urezza; temperature 7·3°; sp. gr. 1·0011; also trace of organic matter.

	CaO.	MgO.	FeO.	K_2O.	Na_2O.	SO_3	SiO_2.	Cl.	CO_2.
I.	6·458	0·483	—	—	—	9·533	0·256	trace	—
II.	2·5175	0·4554	0·0045	0·0594	1·3302	0·3390	0·0265	0·0161	22·8590
III.	7·9970	1·2450	0·1206	0·3779	5·2110	9·2858	0·2450	1·3430	23·3720
IV.	4·6949	0·1559	0·0137	trace	0·0231	6·4873	0·0770	0·0201	1·0695

Analysis is also given of water from a spring at Rhäzüns.

L. J. S.

Physiological Chemistry.

Amount of Hæmoglobin in the Blood at High Altitudes. By PIERO GIACOSA (*Zeit. physiol. Chem.*, 1897, **23**, 326—342).—The method of estimating hæmoglobin adopted was a colorimetric one, the instrument used being a new one, which is fully described and figured.

The results show that a long stay at great altitudes causes an appreciable increase in the blood pigment. A shorter stay so that acclimatisation does not occur, or a longer stay at lower elevations,

causes little or no change; the variations are small, and differ in different species of animals and in different animals of the same species; in man there is a tendency to increase. W. D. H.

Absorption of Iron and Synthesis of Hæmoglobin. By JUSTUS GAULE (*Zeit. Biol.*, 1897, **35**, 377—393).—The presence of iron in the chyle after the administration of inorganic salts of iron is regarded as evidence that the iron is absorbed. In rabbits, this is followed by a marked and rapid rise in the number of blood corpuscles, and of the percentage of hæmoglobin in the blood. The spleen increases in weight, and microchemical examination of this and other organs shows that the synthesis of new blood pigment probably occurs principally in the spleen, and, to a less extent, in the liver and bone marrow. W. D. H.

Reducing Substances in the Blood. By VALDEMAR HENRIQUES (*Zeit. physiol. Chem.*, 1897, **23**, 244—257).—The experiments performed on the blood of dogs and rabbits show that, in addition to the glucose preformed in it, the blood will yield an extra amount after boiling with sulphuric acid; this comes from jecorin; in fact, the sugar which originates from jecorin is from three to five times as abundant as that which is already preformed. W. D. H.

Animal Life without Bacteria in the Alimentary Canal. By GEORGE H. F. NUTTALL, and HANS THIERFELDER (*Zeit. physiol. Chem.*, 1897, **23**, 231—235).—Previous portions of this research have shown that, in mammals, healthy life is possible without the presence of becteria in the alimentary tract. The present observations made on hen's eggs were undertaken with the hope of finding no bacteria in the interior of the egg shell in fresh eggs, and during development. This hope was not fully realised, as the greater number of eggs are infected with bacterial growths, which are derived from the oviduct before and during the formation of the shell.

W. D. H.

Influence of Muscular Exercise, Sweating, and Massage on Metabolism. By JAMES C. DUNLOP, DIARMID NOËL PATON, RALPH STOCKMAN, and IVISON MACADAM (*J. Physiol.*, 1897, **22**, 68—91).—The experiments performed on various human subjects on fixed diet, show that after excessive exercise there is in the urine an increase of total nitrogen (which is chiefly accounted for by increase of urea) of preformed ammonia, of creatinine, and of sulphates (proportionate to the nitrogen). With concomitant sweating, there is diminution of the water, chlorides, and sodium. When the subject is in poor condition, there is a rise of uric acid, nitrogenous extractives, and phosphoric acid.

The general conclusion drawn is that increase of work leads to increased katabolism of the proteid of muscle; this is supported by the fact that uric acid, extractives, and phosphoric acid, are not increased, muscle being poor in nucleo-proteids. The importance of such a conclusion on the training of athletes is pointed out. Experiments on massage gave negative results. W. D. H.

Acetone as a Metabolic Product. By H. CHR. GEELMUYDEN (*Zeit. physiol. Chem.*, 1897, **23**, 431—475).—Acetonuria occurs when insufficient carbohydrate food is given. 100—200 grams *per diem* are necessary for an adult man. A purely proteid diet produces slight acetonuria. During hunger, or a mixed proteid and fat diet, or a purely fat diet, the acetonuria is considerable. The organism possesses the power of destroying acetone in some degree ; but this is not sufficient to hinder acetonuria if the amount of acetone in the circulating fluids of the body is more than the normal traces. (Compare Hirschfeld, this vol., ii, 422.) W. D. H.

Hepatic Glycogenesis. By DIARMID NOËL PATON (*J. Physiol.*, 1897, **22**, 121—136). —This is a further contribution to the long-sustained controversy between the author and Pavy. Some of the experiments previously published are withdrawn, but the general conclusion is still maintained that the conversion of glycogen into glucose is the result of katabolic changes in the liver substance, and not of the action of an amylolytic zymin (enzyme). W. D. H.

The Mineral Constituents of Human Organs. By WACLAW VON MORACZEWSKI (*Zeit. physiol. Chem.*, 1897, **23**, 483—496).—Previous work has shown that in anæmia the urine is rich in phosphorus and poor in chlorine ; in the blood, the converse is true. In pneumonia, both the urine and blood are poor in chlorine and rich in phosphorus. There is, therefore, in some diseases, a retention of chlorine in the body, but this can only be proved by an estimation of the mineral salts of the organs. The present paper gives numerous analyses relating to this point ; they do not, however, bear out fully the expectations of the author ; they show increase of chlorine in cases of anæmia, and decrease in phosphorus and calcium. The organs are also more watery. W. D. H.

The Mineral Matters in Birds' Bones. By FRANZ DÜRING (*Zeit. physiol. Chem.*, 1897, **23**, 321—325).—Several observers have stated that the amount of mineral matter in the bones of birds is greater than in those of mammals ; Weiske, on the other hand, affirms that the percentage is lower. In the present communication, which gives numerous analyses, it is shown that the whole skeleton of various birds contains less (59—63 per cent.) mineral matter than the bones of mammals, in which the average percentage is 66. These percentages are reckoned for bone free from water and fat. If individual bones are taken, however, the long bones are found to be richer in mineral salts (up to 69 per cent.) than the flat bones, where the highest percentage found was 61. W. D. H.

The Sulphuric Acid in Bone-ash. By CARL TH. MÖRNER (*Zeit. physiol. Chem.*, 1897, **23**, 311—320).—Weiske has stated that the natural substance of bone contains no sulphuric acid ; nevertheless, its ash contains that compound, and this is derived from the sulphur of the organic substratum of osseous tissue called collagen. In the present research, it is shown that if a gas burner is used in the process of incineration, a not inconsiderable quantity of sulphuric acid is derived from the gas. This is, however, not the only source of the

compound, for a small quantity is found when a spirit lamp is employed. This varies in quantity in different bones, and originates from chondroitin-sulphuric acid. W. D. H.

Distinction between Organic and Inorganic Compounds of Iron. By A. B. MACALLUM (*J. Physiol.*, 1897, **22**, 92—98).—In microscopic preparations of tissues, the ammonium sulphide and prussian blue reactions are not always satisfactory in deciding the question whether granules are composed of "organic" or "inorganic" compounds of iron. The best reagent is found to be a 0·5 per cent. aqueous solution of pure hæmatoxylin. This does not affect organic iron compounds, but stains inorganic compounds bluish-black. Ferratin, carniferrin, and peptonates and albuminates of iron give the blue reaction, and are therefore classified as "inorganic." "Organic" compounds may be converted into "inorganic" by the action of acidified alcohol. This, however, is not the case with hæmoglohin and hæmatin. W. D. H.

Iodine in the Hairs. By W. HOWALD (*Zeit. physiol. Chem.*, 1897, **23**, 209—225).—There is no iodine or bromine in normal human hairs; but very soon after the usual medicinal doses of iodide or bromide of potassium, iodine or bromine respectively may be detected in the hairs. This disappears when the drug is discontinued and the hair has been repeatedly cut. The halogen is probably in an organic combination, and is introduced in the new hair which grows during the use of the drug. W. D. H.

The Amount of Iodine in Thyroid Glands. By AD. OSWALD (*Zeit. physiol. Chem.*, 1897, **23**, 265—310).—A very large number of determinations of the amount of iodine in thyroids are given; the greater number of these were human, removed after death from various diseases in different Swiss Cantons. It was found that the amount of iodine in the gland was not inversely proportional to the prevalence of cretinism; in fact, thyroids in cases of cretinism in which the degenerative change had not gone so far as to replace the glandular with connective tissue, often contained more iodine than the healthy organ. The quantity of iodine in the thyroids of both men and animals is in direct proportion to the amount of colloid material in the acini. W. D. H.

Presence of Iodine in the Parathyroid Glandules. By EUGÈNE GLEY (*Compt. rend.*, 1897, **125**, 312—315).—The parathyroid glandules of rabbits were found to contain from 2·5 to 3 times as much iodine as the thyroid glands of the same animals. In the case of dogs, the absolute quantity of iodine in the parathyroid glandules is lower than that in the thyroid glands, but the percentage amount is much higher. It is clear that the glandules must be regarded as forming an important part of the thyroidien system. The exact relation between the gland and the glandules is under investigation. C. H. B.

Chemistry of Spermatozoa. By ALBERT MATHEWS (*Zeit. physiol. Chem.*, 1897, **23**, 399—411).—The spermatozoa of the sea urchin *Arbacia* contain no protamine, but instead a histon-like substance to

which the name *arbacin* is given. The chromatin of these spermatozoa is partly, if not exclusively, a union of nucleic acid with arbacin. The nucleic acid has the same percentage of nitrogen and phosphorus as that obtained from the salmon.

The chromatin of herrings' spermatozoa is a compound of protamine and nucleic acid ($C_{30}H_{57}N_{17}O_6,C_{40}H_{54}P_4N_{14}O_{27}$).

The spermatozoa of the bull and boar contain either protamine or a histon extractable by the use of sulphuric acid. W. D. H.

Physiological Action of Chlorhydrins. By C. R. MARSHALL and H. LL. HEATH (*J. Physiol.*, 1897, **22**, 38—60).—The introduction of chlorine atoms into a fatty compound increases its narcotic power. The toxic power is also increased if the solubility of the compound formed is not diminished. Thus dichlorhydrin is more of an irritant than trichlorhydrin, because it is more soluble; the irritant action is seen in the alimentary canal and kidney. The action on muscular tissue increases with each increment of chlorine; as this action is exhibited also on involuntary muscle, the circulation is enfeebled.

W. D. H.

Behaviour of Phenylglycine and Phenylglycinorthocarboxylic Acid in the Animal Body. By JÖRGEN E. THESEN (*J. Physiol. Chem.*, 1897, **23**, 23—29).—See this vol., i, 618.

Physiological Effects of Extracts of Suprarenal Capsules. By SWALE VINCENT (*J. Physiol.*, 1897, **22**, 111—120).—Large doses of suprarenal extract injected subcutaneously produce muscular weakness and finally paralysis, hæmorrhage in various parts, irregularity in the breathing, and fall of temperature. The paralysis is central.

The cortex of the capsules contains no toxic substance. The toxic material of the medulla is rapidly eliminated, hence the largeness of the dose required. A partial immunity can be set up by giving doses not sufficient to kill. W. D. H.

Antagonistic Action of Digitalis and Nitrites. By C. R. MARSHALL (*J. Physiol.*, 1897, **22**, 1—37).—Digitalis counteracts the effect of members of the nitrite group on blood-vessels, but the influence of the latter in antagonising digitalis is much more powerful.

W. D. H.

Phosphorus in Human and Cow's Milk. By JULIUS STOKLASA (*Zeit. physiol. Chem.*, 1897, **23**, 343—346).—Siegfried states that the phosphorus of human milk is almost exclusively in combination in casein and nucleon (phosphorcarnic acid).

This leaves lecithin altogether out of account. The present analyses show that a litre of human milk contains 0·44 gram P_2O_5, and of cow's milk 1·81 grams; of this 0·153 gram (or 35 per cent.) and 0·091 (or 5 per cent.) respectively are obtained from the lecithin present. This, and other facts render a comparison between milk and embryo-plants interesting. It is stated that phosphorcarnic acid is widely distributed in vegetable organisms, and comes into prominence especially during germination and blossoming. W. D. H.

Asses Milk. By ARTHUR SCHLOSSMANN (*Zeit. physiol. Chem.*, 1897, **23**, 258—264).—Asses milk is white, with a bluish opalescence; it is faintly sweet, like diluted cow's milk; the fat globules as seen under the microscope are scanty in comparison with those in cow's and human milk. One c.c. has an alkalinity equal to 0·404 c.c. of decinormal sulphuric acid, and an acidity equal to 0·06 c.c. of decinormal sodium hydroxide. Its sp. gr. varies from 1·031 to 1·036; it contains,

Dry residue	11·15	per cent.
Ash	0·40	,,
Fat	0·36	,,
Sugar	4·94	,,
Phosphorcarnic acid	0·12	,,
Total nitrogen	0·24	,,

Three-quarters of the proteids consist of caseinogen, the remaining quarter being lactalbumin; these account for 86 per cent. of the nitrogen. The small quantity of fat shows how greatly asses milk differs from human milk, with which it is often compared. W. D. H.

Behaviour of Animal and Vegetable Foods in the Alimentary Canal. Introduction. By WILHELM PRAUSNITZ (*Zeit. Biol.*, 1897, **35**, 287—290). **Vegetable Matter in Human Fæces.** By JOSEPH MOELLER (*ibid.*, 291—315). **Flesh in Human Fæces.** By FRITZ KERMAUNER (*ibid.*, 316—334). **Chemical Composition of the Fæces with Different Diets.** By WILHELM PRAUSNITZ (*ibid.*, 335—354). **Bacteria of Human Fæces.** By HANS HAMMERL (*ibid.*, 355—376).—This forms a series of investigations, microscopical, chemical, and bacteriological, on the composition of human fæces. From the nutritional standpoint, such work is essential for the estimation of the value of a diet. Each paper is prefaced by a summary of previous work on the same subject.

Microscopical examination of the fæces after vegetable diet shows a considerable amount of vegetable *débris*, principally of the nature of membranes, and cellulose. Starch grains, after the administration of potatoes and cereals, are hardly ever found.

After an abundant meat diet, muscular fibres in very small quantities form a constant constituent of the fæces, and the amount was roughly estimated by a microscopical comparison of the fæces with some of the same material intimately mixed with a known quantity of finely divided flesh.

In the chemical investigation of the excrements after diets of various kinds, particular attention is given in the analyses to total solids, nitrogen, fat, and ash. By the use of a diet the constituents of which are almost completely absorbed, like rice, meat, baked finely divided wheat meal, there is in the fæces 8—9 nitrogen, 12—18 ether extract, and 11—15 ash per cent.

In comparison with this "normal," the nitrogen usually falls when the diet is less well absorbed; although in a few cases, when nutriment of high nitrogenous value is given, it rises.

The secretions from the intestines always form a very considerable factor in the composition of the fæces, and the quantity of fæces, therefore, depends on the nature rather than on the amount of the food given,

In some apparent exceptions to these rules, a relatively low percentage of nitrogen is produced by a relative increase of ash and fat.

No characteristic difference between the use of animal and vegetable diet is observable. W. D. H.

Stercorin. By AUSTIN FLINT (*Zeit. physiol. Chem.*, 1897, **23**, 363—367).—Bondzynski and Humnicki have given the name koprosterol to a constituent of human fæces which is derived from cholesterol (Abstr., 1896, ii, 320). It is shown that this is no new material, but is identical with the substance named stercorin by the author, and described by him many years ago. W. D. H.

The Nitrogenous Constituents of the Urine. By WILLIAM CAMERER (*Zeit. Biol.*, 1897, **35**, 206—251).—A large number of observations on human urine, in which the influence of diet, age, work, gout, &c., on the amount of total nitrogen, urea nitrogen, uric acid nitrogen, and nitrogen of alloxuric bases are given. In connection with the estimation of the last-named substances, the rreat discrepancies between the results obtained by previous observers a e pointed out. W. D. H.

Uric Acid Formation in Man. By WILLIAM J. SMITH JEROME (*J. Physiol.*, 1897, **22**, 146—158).—The research relates to the influence of diet on the formation of uric acid. If nuclein is introduced in the food, the alloxan group appears in the urine, partly as uric acid; and the variations in the amount of the latter are believed to be chiefly due to the amount of nuclein in the food. The uric acid passed during fasting is, doubtless, attributable to katabolism of nuclein-holding cells in the body. W. D. H.

Urinary Sediments and Gout. By A. RITTER (Carlsbad) (*Zeit. Biol.*, 1897, **35**, 155—182).—The paper is principally a discussion of the possible ways in which, by an interaction of the phosphates and urates in the urine, free uric acid may be deposited. The views of Garrod in relation to the cause of gout are subjected to criticism. In the tables of analyses given, it is shown that, in many cases in which there is a deposit of uric acid crystals, there is no increase in the absolute amount of uric acid; indeed, in cases where the acid is deposited as urates, the uric acid is more abundant. W. D. H.

Constituents of Urine Precipitated by Phenylhydrazine. By MAX JAFFÉ (*Zeit. physiol. Chem.*, 1897, **22**, 532—537).—*Phenylsemicarbazide from the urine of dogs.*—When the urine of dogs, which have been fed on meat, is treated with phenylhydrazine and acetic acid, a large amount of a yellow, crystalline precipitate is obtained, which proved to be identical with phenylsemicarbazide, first obtained by E. Fischer (*Annalen*, **190**, 130) from phenylhydrazine hydrochloride and potassium cyanate.

The author was unable to isolate this substance from the urine of dogs fed on bread or milk, or from human urine after mixed diet.

Phenylsemicarbazide is produced almost quantitatively on warming a solution of carbamide (10, 5, 3, or 2 per cent.) with phenylhydrazine and acetic acid.

The presence of ethylcarbamide in the urine of a dog could not be

proved, although the isolation of its phenylhydrazine compound was attempted. A. W. C.

Kynurenic Acid. By Achille Capaldi (*Zeit. physiol. Chem.*, 1897, **23**, 87—91).—Haagen has observed that the amount of kynurenic acid in the urine of a dog is lessened when the animal is fed with sterilised instead of raw meat. The author points out that it is impossible to attribute this fact to the decrease of putrefactive matter in the intestine, as this cannot have the least influence on the intensity of the bacteriological decomposition. Nevertheless, experiments were made which prove conclusively that the bacteria of the intestines produce no kynurenic acid nor any substance which, after absorption by the tissues, is changed into this acid. Moreover, kynurenic acid is not formed by the action of the secretion of the pancreas of a dog on proteids, nor is it formed in the intestines themselves. A. W. C.

Kynurenic Acid. By P. Solomin (*Zeit. physiol. Chem.*, 1897, **23**, 497—504).—In the dog, the daily excretion of kynurenic acid and of uric acid vary a great deal; but there is no constant relationship between the two. If isatin is given, it is not excreted as kynurenic acid; tyrosine also is not a parent substance of this acid. If kynurenic acid is given subcutaneously, it is in part excreted in the urine as such; but in men and rabbits the percentage excreted is much less, as they have apparently more power to destroy it. W. D. H.

Alcaptonic Acids. By Karl H. Huppert (*Zeit. physiol. Chem.*, 1897, **23**, 412—416).—In recent cases of alcaptonuria, the acid found has been homogentisic acid; but to this a case recorded by Kirk forms an exception, he having described the acid as uroleucic. From some of the raw material from this case, attempts were made in the present research to obtain homogentisic acid, and it was found; Kirk's case is therefore no exception. Uroleucic acid was, however, found as well, although in smaller quantities. The properties of the two acids are very similar; the former contains two hydroxyl groups, the latter three, two united to the benzene nucleus, the third in a side chain.

Methylated uroleucic acid gives the same oxidation product as methylated homogentisic acid; uroleucic acid is probably dihydroxyphenyl-lactic acid, $C_6H_3(OH)_2\cdot CH_2\cdot CH(OH)\cdot COOH$, and this coincides with the view held as to the origin of homogentisic acid from tyrosine.
W. D. H.

Chronic Oxalic Acid Poisoning. By W. Caspari (*Bied. Centr.*, 1897, **26**, 529—533; from *Inaug. Diss. Berlin*). **Feeding Experiments with Turnip Leaves.** By Nathan Zuntz (*ibid.*, 533—534; from *D. Landwirt*, 1896, No. 74).—Experiments in which rabbits were fed with turnip leaves and meal, with meal, bran, and oxalic acid, with excess of calcium carbonate and hydrogen sodium carbonate, showed that oxalic acid in the form of sodium salt is the most injurious, owing, partly, to loss of lime and consequent weakening of the bones. The calcium salt was least injurious, whilst the turnip leaves, which contain both sodium and calcium oxalate, were less injurious than sodium oxalate, and more so than calcium oxalate. Another rabbit, which

received nearly 200 grams of oxalic acid as calcium salt, was less injured than one which had only 11 grams as sodium salt.

Further experiments, made with dogs, showed that the consumption of oxalic acid gave rise to increased amounts of lime in the fæces and urine. When given for a short time, in small amount, and in a not too soluble form, oxalic acid acts beneficially by increasing the appetite. In larger quantity, it is poisonous, injuring the bones and kidneys, and perhaps the heart.

Zuntz refers to von Nathusius's experiments, in which sheep which received food containing oxalic acid for 6 months were not injured; this was shown to be due to the destruction of the oxalic acid in the sheep's rumen. The contents of the rumen of a sheep which had been fed with oxalic acid destroyed a measured quantity of sodium oxalate in 24 hours [the amount is not stated]. Sheep which have not been fed with oxalic acid have not this power, or at least not to the same extent.

With pigs, the same results were obtained as with rabbits and dogs; the bones became so weak that the animals could scarcely stand, and the solid excrement contained large amounts of lime. N. H. J. M.

Clinical Significance of Lactic Acid. By J. H. de Jong (*Chem. Centr.*, 1896, ii, 806—807. See this vol., ii, 607).

Chemistry of Vegetable Physiology and Agriculture.

Behaviour of Yeast at a High Temperature. By T. NAKAMURA (*Bull. Coll. Agric. Imp. Univ. Tokyo*, 1897, **3**, 227—230).—A pure cultivation of yeast was grown in a solution of cane-sugar (10 per cent.) and meat extract (0·5 per cent.), the supernatant liquid poured off, and the sediment washed with sterilised distilled water. It was then suspended in sterilised water, and 5 c.c. of the mixture placed in a test tube closed with a cotton plug, and exposed for several minutes to a constant temperature. The yeast was not destroyed by exposure for $1\frac{1}{2}$ hour at 46°, or for 2 hours at 48°, but was completely destroyed by a temperature of 52° in 20 minutes. Exposure to a temperature of 50° destroyed the yeast in 30 minutes, but not in 29 minutes.

The results of other observers, who state that yeast is destroyed at 40°, is ascribed to the fact that, after being heated, yeast never produced fermentation in Pasteur's solution as quickly as the control sample, the retardation sometimes amounting to several days.

As regards the effect of different compounds in enabling yeast to resist the action of heat, experiments were made in which the yeast was suspended in various solutions and heated at 50° for 30 minutes, and the effect, after addition of sterilised Pasteur's solution, observed. With distilled water, cane-sugar solution (10 per cent.), sodium sulphate (1 to 10 per cent.), and disodium phosphate (1 to 10 per cent.), there was no fermentation; with sodium chloride (1 to 10 per cent.), there was only fermentation after heating in the 3 per cent. solution; with sodium nitrite (1 to 10 per cent.), there was only fermentation in

the case of the 2 per cent. solution; with meat extract (0·5 per cent.), there was normal fermentation. Only the last three solutions had, therefore, the effect of increasing the resistance towards heat.

OSCAR LOEW (*ibid.*, 230—232) calls attention to the soluble proteid recently obtained by Buchner by expressing yeast (this vol., ii, 154). He considers it probable that the proteid is intimately connected with the living protoplasm, and that the greater part of it remains within the cells, where most of the sugar would be fermented. It will be of interest to examine the effect of diamide, hydroxylamine, hydrogen cyanide, &c., on the zymase, on the one hand, and of cyanogen, formaldehyde, &c., on the other (compare Loew, *Pflüg. Arch.*, **27**, 208, and Abstr., 1888, 607). N. H. J. M.

Two New Kinds of Red Yeast. By K. YABE (*Bull. Coll. Agr. Imp. Univ. Tokyo*, 1897, **3**, 233—236).—The two new species of yeast were obtained from the soil of rice fields and from rice straw. They both resemble *Saccharomyces rosaceous* in not forming ascospores, but differ from it in other respects.

Saccharomyces Japonicus.—The cells are elliptic, and approach a more globular form when well nourished with meat extract. Size $= 6 \times 3\ \mu$ (in Pasteur's solution) and $9{\cdot}2 \times 5{\cdot}1\ \mu$ to $10{\cdot}3 \times 6{\cdot}1\ \mu$ (in meat extract). It grows well on potato, and acquires a brilliant red tint. It is unable to produce alcohol from glucose or cane-sugar, and its development is retarded in presence of 3 per cent. of alcohol, and altogether stopped by 7 per cent. A temperature of 45° for 15 minutes destroys the cells.

S. Keiskeana.—Globular cells 5·1 μ to 9 μ in diameter. It forms a faintly pink deposit in Pasteur's solution, but the colour is brighter on potato, probably owing to the effect of free oxygen. A moderate growth is obtained in starch-culture in sugar-gelatin, but the cells remain colourless, whilst those on the surface gradually acquire a pink colour. The cells are killed by heating for 15 minutes at 50°, but not at 46°. Development is retarded by 5 per cent. and stopped by 7 per cent. alcohol. N. H. J. M.

Production of Carbon Bisulphide by Schizophyllum lobatum. By F. A. WENT (*Chem. Centr.*, 1896, ii, 939; from *Ber. deut. bot. Ges.*, 1896, 158—163, and *Centr. Bakt. Par.*, **2**, ii, 528).—A cultivation of *Schizophyllum lobatum* in sugar-peptone yielded carbon bisulphide when distilled; in hydrogen, the fungus produces no carbon bisulphide, or only traces. When cultivated, with peptone as the source of nitrogen, an alcohol (probably ethylic alcohol) is formed, and in absence of air, there is active fermentation, the amount of carbonic anhydride produced being considerably greater than with access of air.

The fungus occurs in Java on old, fallen branches of *Pedocarpus*, and on dead bamboo stems, &c. N. H. J. M.

Decomposition of Fibrin by Streptococci. By OSKAR EMMERLING (*Ber.*, 1897, **30**, 1863—1868. Compare this vol., ii, 113).—The experiments were made with pure cultures of *Streptococcus longus Petruschky*, and with fibrin from the blood of freshly-killed pigs. Four kilograms of fibrin were added to 3 litres of water, and the

whole sterilised by heating at 100° for 2 hours a day during 4 days; the mixture was then inoculated and kept in an incubator at 40° for 3 weeks, when the products of decomposition were investigated. For this purpose, the liquid, after filtration through a Pukall's filter, was distilled at 40° under diminished pressure; the solution, which was faintly alkaline at the beginning, became acid, whilst the distillate was strongly alkaline, and from it the author obtained ammonia, methylamine, and trimethylamine. The following substances were obtained from the residue after evaporation: tyrosine, leucine, acids of the fatty series from acetic to caproic (with the exception of valeric acid), succinic acid, trimethylamine, and a basic substance having the composition of a collidine, although apparently differing from any of those already known. Peptonic substances were also obtained, and their physiological action tested. No poisonous substances could be isolated by the method described. J. J. S.

Decomposition of Elastin by Anærobic Micro-organisms. By LUIGI ZOJA (*Zeit. physiol. Chem.*, 1897, **23**, 236—243).—Elastin was prepared from the *ligamentum nuchæ* of the ox, by a method which differs only in small details from that adopted by Horbaczewski and by Chittenden and Hart. The putrefaction was carried out in a Hoppe-Seyler flask, air being excluded; the gases obtained consisted of carbonic anhydride 90·46, hydrogen 4·74, methane 2·37, and nitrogen 2·43 per cent. Two days after the evolution of gas ceased, the experiment was stopped, and much material was still undissolved; the sulphur is eliminated as mercaptan and not as hydrogen sulphide. In the distillate, valeric and butyric acids were found, whilst the residue gave phenylpropionic acid, aromatic hydroxy-acids, and ammonia.

W. D. H.

Chemical and Bacteriological Investigation of the Fermentation of Fresh Grass. By OSKAR EMMERLING (*Ber.*, 1897, **30**, 1869—1870).—Freshly cut grass was pressed into a large earthenware vessel, closed by a lid into which fitted a thermometer and delivery tube. The composition of the grass was: woody tissue 26·4, ether extract 1·86, proteids 11·8, ash 7·62, and non-nitrogenous extract 52·32 per cent., calculated on the dry substance. At the end of 24 hours, the temperature had risen to 26°, at which point it remained stationary for some time, and then gradually sank to the temperature of the room. For 4 weeks, a slow but continuous evolution of gas, consisting of 64 per cent. carbonic anhydride and 36 per cent. nitrogen, took place. At the end of this period, the grass had the composition: woody tissue 31·36, ether extract 3·24, proteids 9·13, ash 8·14, and non-nitrogenous extract 48·13 per cent. The increase in the ether extract was largely due to the presence of organic acids, formed mainly at the expense of the non-nitrogenous extract, that is, carbohydrates. The hay thus formed possessed a somewhat pleasant ethereal odour, and at the same time a pungent odour which was found to be due to quinone.

Among the organisms isolated were small quantities of moulds, chiefly species of *mucor*; and, besides hay bacteria, granulobacter and coccus species, *Bacillus mycoides* was found. It has been shown that

the latter organism is capable of fermenting glucose, yielding inactive lactic acid; and that it is also capable of hydrolysing cane-sugar, maltose, and glycogen. No other lactic acid bacterium could be isolated.

J. J. S.

An Important Function of Leaves. By U. SUZUKI (*Bull. Coll. Agric. Imp. Univ. Tokyo*, 1897, 3, 241—252).—As it is known that, during the night, a considerable amount of carbohydrates in the leaves migrate to other parts of the plant, it seemed probable that a corresponding amount of proteids are also transported from the leaves, since the decrease of the protecting carbohydrates must involve an attack on the reserve of proteids formed during the day. One experiment has already been made in this direction by Sapoznikow (Abstr., 1896, ii, 537).

The following results were obtained with the leaves of a number of plants which were cut at 6 a.m. and 6 p.m. respectively. The plants selected for experiment were: (1) *Wistaria brachybotrys*; (2) *Phaseolus mungo*; (3) *Phaseolus vulg.*; (4) *Pueralia Thumbergiana*; (5 and 6) *Solanum tuberosum*; (7) *Batatas edulis*; (8) *Polygonum fagopyrum* and (9) *Helianthus annuus*. The numbers show the absolute amounts (in grams) in 100 leaves.

	Evening.					Morning.				
	N.	N. as proteids.	N. as asparagine	N. as amides.*	Starch.	N.	N. as proteids.	N. as asparagine.	N. as amides.*	Starch.
1.	0·1725	0·1457	0·0050	0·218	0·4848	0·1490	0·1215	0·0058	0·0217	0·2611
2.	0·8160	0·6610	0·0300	0·1250	2·0520	0·7270	0·5955	0·0170	0·1145	1·4560
3.	0·8660	0·7021	0·0510	0·1129	5·8970	0·8290	0·6260	0·0490	0·1540	3·9350
4.	1·887	1·516	0·112	0·126	—	1·797	1·559	0·112	0·260	—
5.	0·3350	0·2517	0·0230	0·0603	0·9600	0·3067	0·2390	0·0163	0·0514	0·4134
6.	0·1944	0·1552	0·0130	0·0260	—	0·1791	0·1414	0·0235	0·0142	—
7.	1·566	1·238	0·152	0·176	—	1·504	1·186	0·210	0·108	—
8.	0·1798	0·155	0·0091	0·0156	—	0·1649	0·1435	0·0048	0·0166	—
9.	3·976	2·990	0·226	0·760	7·066	3·590	3·000	0·344	0·246	5·535

* Excluding asparagine.

The results show in most cases a decrease of total and proteid nitrogen, more or less corresponding with the loss of starch. The exceptions in the case of *Helianthus* (9) and *Pueralia* (4) are explained by the fact that the evening leaves were not dried immediately and had therefore remained alive during the night, so that a decomposition of proteids might have occurred with accumulation of amides. This was shown by another experiment to actually take place.

It is therefore established that leaves possess the important function of facilitating the formation of proteids in all parts of the plant by assimilating nitrates, yielding thereby amido-compounds. A great advantage is thus gained for the stems, roots, and fruit, in which the conditions for the assimilation of nitrates are less favourable than in the leaves.

The author thinks that Kosutany's results (this vol., ii, 115) cannot be considered conclusive as regards the functions of leaves under discussion. Kosutany collected leaves at 4 p.m. and at 3 a.m. and the results would therefore show smaller differences than in the present case.

N. H. J. M.

Production of Sugars in Beetroot. By FRIEDRICH STROHMER (*Chem. Centr.*, 1896, ii, 847—848; from *Oestr.-ung. Zeit. Zucker.-Ind. u. Landw.*, **25**, 589—600).—The opinion expressed 30 years ago by H. Schacht, that the quality of beetroots depends on the number of developed leaves and the length of life of the plant, is now shown to be free from objections. Sugar is produced in the leaves either directly as reducing sugar, or from starch or other carbohydrate, and migrates through the leaf stems to the root. The production of sugar depends on the amount of light, and the form and position of the leaves are of importance. When the sunlight passed through white or yellow glass, leaf production was vigorous, but with blue or red glass, feeble; and the weight of roots under the influence of yellow light was nearly twice as great as when blue and red light were employed. The percentage of sugar under the different conditions was 7·4—8·1 with yellow, 6·4—7·4 with red, and 8·0—8·4 with blue light. For producing total organic substance in beetroot, rays of medium wave-length are the most favourable, but for converting the products of assimilation into sugar, the so-called chemical rays seem to have a prominent *rôle*.

The results of field experiments showed that sugar production begins at an early stage in the leaves, but is greatest from the beginning of August to the middle of September. Under favourable conditions, there may be a not inconsiderable accumulation of sugar even later.

From the beginning of July, the sum of the percentages of water and sugar in the roots is constant. This, and the fact that the percentage of sugar in the roots increases until the leaves die, indicates that the sugar, once stored in the roots, remains there. It is only when the roots are taken out of the soil and the leaves cut off that the sugar begins to be used up in maintaining the life of the plant and in preparation for second year's growth. N. H. J. M.

The Carbohydrates of Rye, Barley, and Wheat at Different Periods. By H. JESSEN-HANSEN (*Bied. Centr.*, 1897, **26**, 630—636; from *Carlsberg. Lab. Meddel.*, 1896, **4**, 145—193).—The grain at the dates on which they were examined had the following weights per 200 (in grams). I. Rye (*a*) 20—22 June, 1893, 2·486; (*b*) 29—30 June, 5·1255; (*c*) 11 July, 9·561, and (*d*) 22 July, 9·505. II. Barley (*a*) 29—30 June, 6·377; (*b*) 3 July, 10·684; (*c*) 14 July, 20·216, and (*d*) 25 July, 19·450. III. Wheat (*a*) 4 July, 5·193; (*b*) 13 July, 9·900, and (*c*) 31 July, 14·300 grams. The following table gives the analytical results at the different dates.

	Dry matter in fresh grains.	Per cent. in dry substance.								
		Pentosans.	Starch.	Sol. in 90 per cent. alcohol.			Soluble in 70 per cent. alcohol.			
				Invert-sugar.	Cane-sugar.	? Secalose.	Invert-sugar.	Cane-sugar.	Baryta prop.	"Unknown."
I. *a.*	27·6	5·1	(11·4)*	5·15	5·23	7·78	0·90	0	19·40	6·36
b.	33·0	7·6	34·8	3·5	2·52	1·78	0·38	0	9·62	4·82
c.	45·4	7·4	50·9	0·98	1·47	0·68	—	0·50	0·11	1·68
d.	58·45	6·4	60·6	0·31	0·43	0·34	0·36	0·74	trace	1·94
II. *a.*	24·39	3·5	16·08	5·14	9·15	6·10	0·98	0	9·05	7·21
b.	28·60	4·1	40·40	1·84	2·74	3·03	0·67	0	7·4	5·25
c.	40·41	5·8	57·42	0·50	0·44	0·55	0·57	0·09	trace	1·31
d.	55·60	5·7	57·57	—	—	—	0·68	0·47	0	0·54
III. *a.*	27·85	5·4	26·45	5·20	5·56	8·46	1·23	0	6·81	4·45
b.	37·77	7·0	54·45	1·14	1·27	0·71	0·36	0	2·54	2·96
c.	55·29	6·4	65·90	0·48	0·44	0·33	0·39	0	trace	1·15

* Determination made in sample taken 20 June, 1894.

The precipitate obtained with baryta from the rye extract yielded a substance, probably identical with Tanret's levosin, which the author terms *apeponin*; this compound has the formula $(C_{12}H_{22}O_{10})_2$, decomposes at 128—130° without discoloration, and melts at about 230°, darkening at the same time. Its specific rotatory power is about $-41·3°$. It does not ferment, and does not reduce alkaline copper solutions.

Barley grain yielded the same constituents as rye, namely, glucose, fructose, cane-sugar and apeponin. Raffinose could not be detected.

In the case of wheat, only the reducing sugars, and apeponin, were identified with certainty.

Oats were also analysed at different dates; but only pentosans and starch were determined. Single grains weighed as follows:—(*a*) 7 July, 17·4; (*b*) 15 July, 34·0; (*c*) 28 July, 51·6, and (*d*) 10 August, 33·8 milligrams. The results were as follows:—

Dry matter per cent.				Pentosans per cent. in dry matter.				Starch per cent. in dry matter.			
a.	*b.*	*c.*	*d.*	*a.*	*b.*	*c.*	*d.*	*a.*	*b.*	*c.*	*d.*
41·8	36·6	52·9	84·8	27·2	19·5	11·3	12·7	2·8	11·6	40·5	42·3

Apeponin could not be detected in oats, even at the earlier stages of growth. N. H. J. M.

Behaviour of Active Albumin as Reserve Material during Winter and Spring. By U. SUZUKI (*Bull. Coll. Agric. Imp. Univ. Tokyo*, 1897, **3**, 253—258).—Daikuhara (Abstr., 1895, 128) showed that the leaves of plants which contain active albumin in the summer, also contain it in October and November, although usually in far less amount.

The examination of the bark and buds (in March, before the buds had opened) of 48 species, showed, in 25 cases, the presence of active albumin; frequently the bark contained more than the buds. Active albumin, therefore, resembles other reserve substances in being stored up in the bark of trees. N. H. J. M.

Formation of Proteids in Plants by the Reduction of Nitrates. By EMIL GODLEWSKI (*Ann. Agron.*, 1897, **23**, 310—324; from *Anzeiger Akad. Wiss. Krakau,* 1897, 104—121).—Seedlings of wheat were cultivated in solutions, both with and without nitrate, some in the dark, others exposed to light. The latter were under glass shades through which air free from carbonic anhydride passed. After three weeks, the plants were removed, weighed, dried, and analysed.

There was a loss of dry substance in every case, rather greater in the case of the plants exposed to light than in those grown in darkness. The amount of nitrogen in different forms in the grains and plants (taking the total nitrogen of the seeds as 100) was as follows. (Experiments 1—3 were made in diffused daylight, 4—7 in the dark. 1, 2, 4—6 were supplied with nitrate, 3 and 7 were without nitrate.)

	Total nitrogen.	Total organic nitrogen.	Nitrogen as proteids.	Soluble proteid nitrogen.	Insoluble proteid nitrogen.	Nitrogen as amides and ammonia.	Nitrogen as nitrates.
In seeds	100	100	92·68	74·04	18·64	7·32	0
1 with nitrate	218·72	179·97	119·14	100·19	18·95	60·83	38·75
2 with nitrate	206·04	149·63	108·58	90·05	18·53	41·05	56·41
3 without nitrate	95	95	67	55	12	28	0
4 with nitrate	154·16	113·77	76·07	51·73	24·34	37·70	40·39
5 with nitrate	177·11	123·26	70·75	54·53	16·22	52·51	53·85
6 with nitrate	174·79	122·44	71·96	55·16	16·80	50·48	52·35
7 without nitrate	92·73	92·73	61·67	45·05	16·62	31·06	0

The results show that, both in diffused daylight and in absence of light, the plants accumulated considerable amounts of nitrates. Proteids were produced, under the influence of light, when nitrates were supplied; in the dark, formation of proteids from nitrates did not take place to any extent, if at all. Proteids are not formed directly from nitrates; non-proteid compounds are first produced which are subsequently converted into proteids, these non-proteid compounds being formed both with and without the aid of light, and in much greater quantity when nitrate is supplied than without nitrate. Light is necessary for their transformation into proteids. (Compare Laurent, Marchal, and Carpiaux, *Bul. Acad. roy. Belg.*, [iii], **32**, 816—865; and Hansteen, *Ber. deut. bot. Ges.*, 1896, **14**, 362.) N. H. J. M.

A Compound rich in Manganese obtained from Woody Tissue. By GABRIEL GUÉRIN (*Compt. rend.*, 1897, **125**, 311—312).—When wood sawdust is macerated for two or three days with a 1 per cent. solution of potassium hydroxide, a deep brown liquid is obtained, and when this is acidified with hydrochloric acid, a bulky, flocculent precipitate is produced. This precipitate can be washed with very dilute hydrochloric acid, redissolved in ammonia, reprecipitated by acid, washed and dried. It is a pale brown powder, which, when

obtained from the beech, had the composition, C, 52·762; H, 5·04; N, 4·60; S, 0·666; P, 1·297; Mn, 0·402 per cent. C. H. B.

Volatile Reducing Substance of the Green Parts of Plants. By THEODOR CURTIUS and J. REINKE (*Bied. Centr.*, 1897, **26**, 573; from *Ber. deut. bot. Ges.*, 1897, 201, and *Rep. Chem. Ztg.*, 1897, 133).—In accordance with Baeyer's theory, Reinke detected, some years ago, an aldehydic substance in chlorophyllous plants which does not occur in fungi.

By distilling leaves with steam, and treating the distillate with a hot, saturated alcoholic solution of metanitrobenzhydrazide, a small quantity of flakes of a microcrystalline precipitate was obtained. This compound of an aldehyde alcohol with 1 mol. nitrobenzhydrazide, is soluble in water, and readily soluble in cold absolute alcohol; the *aldehyde alcohol* itself, $C_7H_{11}O{\cdot}CHO$, is supposed to be the reducing substance of green leaves. N. H. J. M.

Production of Ammonia from Vegetable Substances and Humus. By ÉMILE BRÉAL (*Ann. Agron.*, 1897, **23**, 356—369).—Nettles kept for three hours in carbonic anhydride, and then distilled with magnesia, yielded ammonia, whilst a similar plant which had been kept in air did not. Ammonia was also obtained from clover and lucerne, and from maize after treatment with chloroform or ether; vegetable substances, when dried in confined air, likewise yielded ammonia.

Poa annua, when kept in water covered with a shade through which air was passed, did not give off ammonia, but the same plant, after the roots were cut off, yielded ammonia in the course of 24 hours. The water in which vegetable matter has been kept is capable of inducing ammonia production from other substances, such as wool, horn, leather, &c. Soil humus gives off ammonia after contact with a leaf taken from a fermenting vegetable infusion.

Plants may induce the production of ammonia in the soil in contact with their roots, and absorb the ammonia thus liberated. N. H. J. M.

Occurrence of Amines in the Juice of the Sugar-Cane. By J. L. BEESON (*J. Amer. Chem. Soc.*, 1896, **18**, 743—744).—Although the products of the sugar-beet have long been known to contain amines, their presence in the juice of the sugar-cane has not hitherto been recognised. By heating the precipitate formed on adding lime water to sugar-cane juice, the author has obtained a product which possesses the general properties of an amine. E. W. W.

Bisabol-Myrrha. By W. TUCHOLKA (*Arch. Pharm.*, 1897, **235**, 289—301).—An analysis of bisabol-myrrha obtained from Somaliland gave the following results. Gum soluble in water, 22·1; gum soluble in soda, 29·85; resin, 21·5; bitter principles, 1·5; ethereal oil, 7·8; water, 3·17; and inorganic matter, &c., 13·4 per cent. The ethereal oil, when dissolved in ether and saturated with gaseous hydrogen chloride, yielded a dextrorotatory compound of the formula $2(C_{10}H_{16},2HCl)$, forming hexagonal plates, and melting at 79·2°. This, on treatment with anhydrous sodium acetate and glacial acetic acid, gave the *hydrocarbon*, $C_{10}H_{16}$, having a sp. gr. = 0·8914 at 17°, a refraction $n'_D = 1·4608$ at 17°, and a dispersion = 0·01186 at 17°; the molecular

refraction therefore = 44·17, from which it appears that the compound contains two double bonds. An oil boiling at 230—231°, and of the formula $C_{56}H_{96}O$ was isolated from the residue after treating it with hydrogen chloride; the matter is still under investigation.

J. F. T.

Physiological Action of Disodium Sulphite on Phænogams. By K. NEGAMI (*Bul. Coll. Agric. Imp. Univ. Tokyo*, 1897, **3**, 259—264).—The fact that amidosulphonic acid is innocuous to lower vegetable and animal life, but poisonous to phænogams (this vol., ii, 279) suggested the possibility that the effect on the latter might be due to the production of sulphurous acid.

Experiments in which onion and barley plants, branches of *Prunus Persica* and *P. triflora*, leaves of *Heliotropium Peruvianum* and *Vitis incrustans*, and seeds of radish, barley and soja bean were subjected to the action of disodium sulphite (1 per cent.) showed that the salt is poisonous to the developed plants but does not injure radish and barley seeds. The germination of soja bean was, however, very much retarded, possibly owing to the oxygen dissolved in the water being absorbed by the sulphite. Further experiments will have to be made to decide whether the action of the sulphite accounts for the injurious effect of amidosulphonic acid.

N. H. J. M.

Poisonous Action of Ammonium Salts on Plants. By S. TAKABAYASHI (*Bul. Coll. Agric. Imp. Univ. Tokyo*, 1897, **3**, 265—274).—Many plants develop better when manured with nitrates than with ammonium salts, and whilst nitrates may be stored up in plants to a considerable extent, ammonium salts are not, most of the excess being converted into asparagine (Kinoshita, Abstr., 1896, ii, 54).

Ammonium carbonate (0·5 per cent.) kills vegetable objects in a few days, and 0·05 per cent. solutions have the same effect but more slowly. Whilst the poisonous effect of the stronger solution cannot be counteracted, the noxious effect of the weaker solution can be retarded, in many cases, by the presence of cane-sugar or glycerol. Ammonium sulphate is much less poisonous than the carbonate.

Two sets of barley plants (one of which had been exhausted of reserve material, and the other kept in direct sunlight in 1 per cent. cane-sugar) were placed in solutions of (1) ammonium carbonate, (2) ammonium chloride, (3) ammonium sulphate, and (for control) (4) sodium carbonate, (5) sodium chloride, and (6) water; the solutions were of two degrees of strength, 0·1 and 0·5 per cent. During the experiment, the plants were kept in the dark. A second and third series of experiments included onions and wheat respectively, as well as barley.

The results confirmed the poisonous effect of ammonium salts in absence of sufficient sugar in the plant. In well-nourished plants, the noxious effect of ammonium salts is not noticed, owing to their conversion into asparagine.

N. H. J. M.

Injury to Rye by Perchlorate contained in Nitrates. By By B. SJOLLEMA (*Ann. Agron.*, 1897, **23**, 328—329; from *Deut.*

landw. Presse., 1897, No. 3).—In Holland and Belgium, rye crops which had been manured with sodium nitrate were more or less damaged. In some cases, the plants, after a few weeks, seemed scorched; in other cases, where the injury was less, the growth was stunted and seed production imperfect. A number of samples of the nitrate were examined and found to contain from 0·14 to 6·79 per cent. of perchlorate, and nearly corresponding amounts of potash. Direct experiments with sodium and potassium perchlorates showed that these salts retard germination and cause the leaves of plants to which they were applied to become yellow.

It is concluded that 200 kilos. of sodium nitrate (? per hectare) containing 0·5 per cent. of perchlorate would be injurious.

Dehérain mentions that Muntz (*Ann. Chim. Phys.*, [vi], **11**, 111; and Abstr., 1895, 870) showed that iodides and bromides are oxidised by nitrifying organisms to iodates and bromates respectively, whilst attempts to convert chlorides into chlorates failed. It is still unknown whether the perchlorates found in sodium nitrate could have been produced by micro-organisms. N. H. J. M.

Nitrogen Nutrition of the Leguminosæ. By KARL VON ROZDEJCZER (*Inaug. Diss. Leipzig*).—Peas were grown in sandy soil (N = 0·0128 per cent.), in loamy soil (N = 0·122), and in humus soil (N = 0·214 per cent.), in pots containing respectively 18·66, 14·66, and 12·82 kilograms of dry soil. There were three series of experiments, (1) unmanured, (2) with minerals and sodium nitrate (N = 0·3048 gram per pot), and (3) with minerals alone. The pots were in the open air except in very wet weather, and the amount of nitrogen in the rain and in the water used was determined; there were three or four plants to each pot. On taking up the plants, the greatest nodule development was found in the pots which had received mineral manure, and in the unmanured sandy soil; the development was only slight in the loamy and humus soils, and very slight under the influence of sodium nitrate. The following summary shows the average amount of nitrogen (in grams) per pot, in the seeds sown in the soil, and in the produce, and also the gain or loss at the end of the experiment.

				In soil.				Total.		
Pots.				Initial.*	Final.	In seed.	In produce.	Initial.	Final.	Gain or loss.
1—3	Sandy	soil;	no manure...	2·4333	2·4342	0·0321	0·2544	2·4654	2·6886	0·2232
8, 9, 11	,,	,,	sod. nitrate	2·7381	2·4656	0·0321	0·3744	2·7702	2·8400	0·0698
15—17	,,	,,	minerals......	2·4333	2·4342	0·0370	0·3680	2·4703	2·8022	0·3319
4, 6	Loamy	,,	no manure...	18·1838	18·0914	0·0370	0·3222	18·2208	18·4136	0·1928
10, 12	,,	,,	sod. nitrate	18·4886	18·0914	0·0407	0·4148	18·5293	18·5062	−0·0231
5, 7	Humus	,,	no manure...	28·0520	27·9690	0·0333	0·4965	28·0853	28·4650	0·3797
13, 14	,,	,,	sod. nitrate	28·3568	28·0995	0·0333	0·3375	28·3901	28·4370	0·0469

The results show a gain of nitrogen in each set, except in the case of the loamy soil which received nitrate, and in this there was a loss; the loss was in pot 10; in pot 12, there was a gain of nitrogen (= 0·0276).

It is concluded that, with insufficient nitrogen in the soil, peas assimilate considerable amounts of free nitrogen, and thus enrich the soil; but with increased supply of soil nitrogen, this power of fixing free nitrogen diminishes, the plant utilising the combined nitrogen of the

* Including 0·018 gram in rain, and (Pots 8—14) 0·3048 gram as nitrate.

soil. With rich soil, elementary nitrogen is either not utilised at all or else in very small quantities. Leguminous crops should be well manured with potash and phosphoric acid. N. H. J. M.

The Amount of Nitrogen conveyed by Red Clover to Different Kinds of Soil. By NAPOLEONE PASSERINI (*Bol. Scuola Agrar. Scandicci*, 1895, **3**, 102—111).—Red clover was grown in three different soils contained in wooden boxes 50 cm. square. The soil had the following composition (per cent. in dry soil).

	Sand.	Clay.	Loss on heating.	$CaCO_3$.	N.
1.	54·542	34·670	6·800	1·581	0·1546
2.	85·406	10·528	3·386	0·323	0·1033
3.	40·936	36·180	9·818	13·152	0·1366

Calcium phosphate and sulphate, and potassium chloride were mixed with the soil, each at the rate of 400 kilograms per hectare. Two crops of clover were cut weighing together (1) 223, (2) 312, and (3) 252 grams respectively; or as hay, 39·5, 69, and 76 grams.

At the conclusion of the experiment, the nitrogen of the soil was again determined, with the following results. Nitrogen, in dry soil =(1) 0·1388, (2) 0·0847, and (3) 0·1600 per cent. The total loss or gain of nitrogen is shown below (in grams).

	N. in soil.					Total N.		
	Initial.	Final.	Difference.	N. in seed.	N. in crop.	Initial.	Final.	Loss or gain.
1.	167·673	150·537	−17·136	0·0237	1·2897	167·6967	151·8267	−17·1590
2.	137·969	113·126	−24·843	0·0237	2·1411	137·9922	115·2671	−24·8662
3.	151·978	178·013	+26·035	0·0237	2·4287	152·0021	180·4417	+26·0109

Whilst there was a gain in the calcareous soil (3), under the influence of red clover, in the other two soils there was an actual loss, due in part to the loss of nitrates in drainage, and partly to less active fixation of nitrogen. The results indicate that "sideration" will not be successful in soil poor in lime, even when manured with phosphates and potassium salts. N. H. J. M.

Experiments on the Effect of Magnesia on Wheat. By NAPOLEONE PASSERINI (*Bol. Scuola Agrar. Scandicci*, 1895, **3**, 140—142).—Wheat was sown in three plots of 10 square metres, and manured in the autumn with mineral phosphates, and in the spring with sodium nitrate (80 kilograms per hectare). Magnesium carbonate was applied in quantities of 500 and 200 kilograms per hectare to plots 1 and 2 respectively, whilst none was given to plot 3. The following amounts of produce were obtained (kilograms per hectare).

1. $MgCO_3$, 500 kilos.		1. $MgCO_3$, 200 kilos.		3. Without $MgCO_3$.	
Grain	Straw and chaff.	Grain	Straw and chaff.	Grain	Straw and chaff.
1,900	10,100	2,180	9,320	2,320	9,680

The presence of magnesium carbonate, in the quantities applied, caused, therefore, a diminished yield of grain. The quality of the grain was also injured, the weight per litre in the three experiments

being respectively (1) 766, (2) 770, and (3) 777 grams. (Compare Larbalétrier and Malpeaux, Abstr., 1896, ii, 445.) N. H. J. M.

The Pentosans and Crude Fibre of Various Foods. By FRANZ DÜRING (*Bied. Centr.*, 1897, **26**, 603—605; from *J. Landw.*, 1897, **45**, 79).—The following results are given (per cent. in dry matter).

—	Crude protein N × 6·25.	Ether extract.	Ash.	Crude fibre (free from pentosans).	N-free extract (free from pentosans).	Pentosans. Furfuraldehyde × 1·84.	Dry matter.
Meadow hay ...	11·70	3·60	7·03	21·09	37·63	18·95	93·26
Rye straw	3·24	2·28	4·31	37·61	23·47	29·09	93·20
Clover hay	13·90	2·31	6·01	33·74	28·00	16·04	92·04
Lupin straw . ..	5·80	1·36	3·76	45·34	22·91	20·83	91·56
Sheep fæces	11·89	4·80	12·79	21·16	29·14	20·22	92·80

The results support the view of Pfeiffer and Götz (this vol., ii, 428) that, in herbivorous animals, hippuric acid is derived from pentosans, and this also accords with the observed increased amount of hippuric acid after feeding with oats and oat straw, as compared with food consisting essentially of leguminous corn or straw. N. H. J. M.

Nitrification in Soil. By R. BURRI and ALBERT STUTZER (*Chem. Centr.*, 1896, ii, 113; from *Centr. Bakt. Par.*, **2**, ii, 196—204).—All cultivations which oxidised ammonia to nitrite, contained an organism greatly resembling Winogradsky's *Nitrosomas europæa*, but attempts to obtain pure cultivations on silicic acid plates failed. With regard to the oxidising power of nitrous organisms from different sources (five were from Germany and one from Africa), there seems to be no essential difference. A nitric organism was obtained from Northeim soil which was identical with that obtained by Winogradsky from Quito; when cultivated on gelatin, this organism no longer oxidised nitrites, and only occasionally recovered its nitrifying power when recultivated in mineral matter.

Cultivations containing both nitrous and nitric organisms could be made, by appropriate addition of nitrogenous salts, to nitrify like soil, that is, to apparently produce nitrates directly from ammonia.

N. H. J. M.

Nitrification of the Nitrogenous Matter of Soil and of some Nitrogenous Manures. By PH. BONAME (*Mauritius Rapp. Ann. Stat. Agron.*, 1896).—The soil with which the experiments were made consisted of coarse sand, 2·8; fine sand, 46·3; and clay, 25·5 per cent., with a trace of humus, and contained N = 0·350, CaO = 0·155, and MgO = 0·043 per cent. It is considered a fair sample of the soil of the island where high percentage of nitrogen with low percentage of lime is common.

A number of metallic cylinders were filled with the soil (3 kilograms), (1) alone, and mixed with (2) ammonium sulphate, (3) dried blood, (4) cake, and (5) fish guano respectively. The amount of

nitrogen applied was the same in each case, and amounted to 0·180 per cent. of the soil. There were two cylinders in each experiment, one of which received 5 per cent. of chalk ("sable calcaire" containing $CaCO_3$, 91·1; $CaSO_4$, 0·68; insoluble matter, 1·12; and water, Na_2O, MgO, &c., 7·10 per cent.).

The following table shows the amounts of nitrogen, per million of soil, as ammonia and as nitrites, at the different dates. The experiment commenced 15 April. The numbers 1—5 represent the cylinders without, 1*a*—4*a* the cylinders with chalk, 1*b* was soil to which lime but no nitrogenous manure was added.

	N as NH_3 per million.						N as N_2O_5 per million.					
	11 June.	12 July.	14 Aug.	15 Sept.	26 Nov.	20 Feb.	11 June.	12 July.	14 Aug.	15 Sept.	26 Nov.	20 Feb.
1	5	17	18	25	29	—	42	50	83	83	80	80
1*a*	25	30	25	18	28	—	62	73	60	100	100	110
1*b*	22	46	80	16	35	—	170	200	190	240	280	280
2	1610	1650	1540	1500	1450	1040	220	290	350	440	510	850
2*a*	1020	530	80	40	70	50	750	1330	1860	1900	1870	1880
3	710	730	680	630	510	500	660	740	850	880	1010	1010
3*a*	200	70	40	40	30	50	1230	1510	1590	1580	1740	1780
4	630	550	480	470	130	40	590	820	950	1010	1390	1550
4*a*	260	60	70	20	40	30	970	1390	1370	1480	1550	1660
5	550	400	300	180	40	—	740	1100	1130	1370	1610	1640

The results show a very marked effect produced by chalk on the rate of nitrification, whilst lime, in No. 1*b*, had a still greater effect, although applied in much smaller quantity (1 per cent.). The better results obtained with lime are partly ascribed to its being in a finer state of division than the chalk. Ammonium sulphate nitrified very slowly in absence of chalk, but the addition of chalk to the otherwise unmanured soil did not have much effect on nitrification. Fish nitrified most readily, then cake, dried blood, and ammonium sulphate; probably nitrification is assisted by the presence of calcium phosphate and carbonate in the organic manures. The slow nitrification of ammonium sulphate, and the beneficial results obtained by its application to crops, support the view that, under some conditions, plants may directly utilise ammonium salts.

In another series of experiments, it was found that, with dried blood, with and without chalk, the soil-extracts contained, with chalk, 481 parts of lime and 30 parts of magnesia; without chalk, only 201 and 65 parts of lime and magnesia respectively per 1,000 parts of nitric acid. As, to produce calcium nitrate, 518 parts of lime would be necessary, it is concluded that the excess of nitric acid is present as ammonium salt.

The temperature of Mauritius is favourable to nitrification, the

mean daily temperature of the year being 59° to 90°; and during the warm season, December to June or July, the soil is also sufficiently moist. N. H. J. M.

Fixation and Nitrification of Nitrogen in Arable Soils. By PIERRE PAUL DEHÉRAIN (*Compt. rend.*, 1897, **125**, 278—283).—Arable soil was kept moist and protected from frost, and it was found that, under these conditions, there is not only rapid nitrification even during the winter months, but also a considerable increase in the total nitrogen. In one set of experiments, carried on from November, 1896, to June, 1897, the nitric nitrogen increased from 0·0 gram to 0·390 gram per kilogram, the organic nitrogen from 1·720 to 1·900, and the total nitrogen from 1·720 to 2·290 grams per kilogram. The simultaneous occurrence of rapid nitrification and considerable fixation of atmospheric nitrogen is very noteworthy.

Slow drying of the soil is, as a rule, inimical to nitrification, but the magnitude of the effect varies greatly with different soils; the rapid desiccation that takes place during a drought is, however, almost always decidedly injurious. The conditions most favourable to nitrification and the fixation of atmospheric nitrogen seem to be the maintenance of an equable temperature and a somewhat high degree of humidity. C. H. B.

Increase of the Nitrogen of the Soil by White Mustard. By STANISLAUS VON KOWERSKI (*Inaug. Diss. Halle a. S.*, 1895).—A number of pot experiments were made, in which white mustard was grown in two lots of arable soil, containing respectively 0·1149 and 0·1261 per cent. of nitrogen; there were also two pots with mustard and peas together, as in Liebscher's experiments (Abstr., 1894, ii, 201). The pots held about 14 kilograms of soil, containing about 16 grams of nitrogen. The soil of six of the pots was sterilised, but no attempt was made to maintain sterilisation, and the whole experiment was conducted out of doors. Most of the pots received sodium nitrate (N = 0·5306 and 0·849 gram per pot) as well as mineral manure. Each pot showed a gain of nitrogen, the gain being 2 to 7 times greater in the unsterilised than in the sterilised soil; there was also a greater gain of nitrogen under the influence of nitrogenous manure than when unmanured.

It is concluded that the fixation of free nitrogen took place under the influence of micro-organisms present in the soil, and that the activity of the microbes is assisted both by sodium nitrate and, in rich soil, by vigorous vegetation (such as mustard) which would prevent the microbes becoming injured by excess of combined nitrogen.

White mustard does not itself assimilate elementary nitrogen. Peas growing in rich soil, which only reach the flowering period, do not assimilate free nitrogen even when their roots have nodules.

N. H. J. M.

Conservation of Farmyard Manure. By FRANZ W. DAFERT and R. BOLLIGER (*Rel. Ann. Inst. Agron. Est. São Paulo, Campinas*, 1894—1895, 7 and 8, 175—186).—The object of the experiments was to ascertain the effect of the amount of moisture on the amount of nitrogen

and organic matter of stable manure both with and without addition of gypsum.

Known amounts (about 400 grams) of ass-manure, without and with gypsum (5 per cent.), were kept in cylindrical vessels in the shade, and the amounts of dry matter and nitrogen determined after intervals of 92, 106, 120, and 134 days. At the commencement, the manure contained 22·20 per cent. of dry matter; in the "dry" experiments, the percentage of dry matter rose to 45·9 without, and 69·5 with gypsum, whilst in the "wet" experiments the percentage was maintained at about 12 and 17 respectively. The following numbers show the percentage loss or gain of dry matter and nitrogen during the successive periods.

	Loss of dry substance (per cent.).				Loss of nitrogen (per cent. of total).			
	92 days.	106 days.	120 days.	134 days.	92 days.	106 days.	120 days.	134 days.
Dry: without gypsum ...	42·72	6·42	3·72	2·28	11·16	2·13	0·35	0·61
Moist: ,, ,, ...	45·05	2·70	0·84	0·08	15·54	13·04	2·31	0·10
Dry: with ,, ...	31·38	7·60	5·45	6·30	6·89	+0·17	+0·18	+2·76
Moist: ,, ,, ...	38·55	2·38	0·79	0·08	8·95	7·49	1·40	4·80

It is concluded that the decomposition of manure depends largely on temperature and moisture, a difference of 1°, and of 1 per cent. of water, having a distinct influence. At the commencement, the decomposition of organic matter predominates, whilst the breaking up of nitrogenous compounds follows later. Gypsum, when well mixed with the manure, prevents loss of organic matter and nitrogen. During the first period, dryness favours the preservation of organic matter (yielding inferior manure), whilst moisture (within limits) assists the preservation of the nitrogen, producing manure of good quality. In the second period, excess of water is injurious.

Under certain conditions, not yet understood, there was a gain of nitrogen. N. H. J. M.

Drainage Waters. By Pierre P. Dehérain (*Ann. Agron.*, 1897, **23**, 241—267. Compare Abstr., 1895, ii, 458).—*Results obtained, March*, 1895—*March*, 1896.—The rainfall of this year was nearly equally distributed between the winter and summer months. There was no drainage during the summer through any of the cases. In the spring (May 9), drainage was collected from the fallow cases (1, 12, 13, and 14) and from those planted with vines. The average amount from the fallow cases was 10·1 millimetres (= 0·40 inch), and it contained nitrogen as nitrates corresponding with 9·38 kilograms per hectare (= 8·38 lbs. per acre). From the vine cases, the drainage was less than 1 millimetre, and the loss of nitrogen only 1·195 kilograms per hectare (= 1·07 lbs. per acre). During the winter months, the fallow cases yielded drainage: average of 1 and 13 (not dug) = 72·1 millimetres (2·84 inches), of 12 and 13 (dug) 89·45 millimetres (3·52 inches). The average loss of nitrogen in 1 and 13, and in 12 and 13 respectively was 82·5 kilograms (73·7 lbs. per acre), and 118·68 kilograms per hectare (105·9 lbs. per acre). The character of the produce from the various cases is described, and the amounts given.

Results obtained, March 1896—*March* 1897.—The rainfall of this year was below the average during the early part of the year, but exceptionally high in September and October, making the total amount for the year above the average. The winter was mild. The following table shows the amount of drainage during the year from each case, the amount of produce, and the loss of nitrogen as nitrates in the drainage.

Produce in kilograms per hectare and lbs. per acre.	Drainage.		Nitrogen as nitrates.		
	Mm.	Inches.	Per million.	Kilos. per hectare.	Lbs. per acre.
1. Fallow—not dug	282	11·11	0·074	209·1	186·7
2. Rye grass, 5,325 kilos. = 4,754 lbs.	198	7·80	0·0013	2·6	2·3
3. Oats, grain, 19·5 q. met. = 1,741 lbs.; straw, 45·2 q. m. = 4,036 lbs.	185	7·29	0·0044	8·3	7·4
4. Oats, grain, 18·3 q. met. = 1,634 lbs.; straw, 42·5 q. m. = 3,794 lbs.	201	7·92	0·007	14·2	12·7
5. Oats, grain, 18·3 q. met. = 1,634 lbs.; straw, 42·5 q. m. = 3,794 lbs.	204	8·04	0·013	26·2	23·4
6. Maize: green fodder = 70,000 kilos. = 62,500 lbs.	176	6·93	0·014	24·2	21·6
7. Maize: green fodder = 71,250 kilos. = 63,616 lbs.	169	6·66	0·009	16·5	14·7
8. Maize: green fodder = 75,000 kilos. = 66,964 lbs.	167	6·58	0·018	28·7	25·6
9. Wheat: Vetches: grain = 20·75 q. = 1,853 lbs.; straw, 42·5 q. = 3,794 lbs.; vetches = 7,500 k. = 6,696 lbs.	168	6·62	0·009	14·4	12·8
10. Wheat: grain = 20·2 q. = 1,803 lbs.; straw, 42·75 q. = 3,817 lbs.	190	7·49	0·017	33·3	29·7
11. Wheat: Vetches: grain = 16·0 q. = 1,429 lbs.; straw, 42·5 q. = 3,794 lbs.; vetches = 6,500 k. = 5,803 lbs.	174	6·86	0·005	7·9	7·1
12. Fallow—dug	293	11·54	0·075	220·2	196·4
13. ,, not dug	283	11·15	0·062	176·9	157·9
14. ,, dug and rolled	285	11·23	0·072	205·2	183·2
15. Potatoes: tubers, 27,500 kilos. = 24,553 lbs.	148	5·83	0·014	27·7	24·7
16. Vines: vintage, 18,800 kilos. = 16,786 lbs.	189	7·45	0·022	40·8	36·4
17. Vines: vintage, 18,950 kilos. = 16,920 lbs.	188	7·41	0·045	84·0	75·0
18. Sugar beet: roots, 28,000 kilos. = 25,000 lbs.	182	7·17	0·0014	2·7	2·4
19. Sugar beet: roots, 32,750 kilos. = 29,241 lbs.	182	7·17	0·0002	0·3	0·3
20. Sugar beet: roots, 31,250 kilos. = 27,902 lbs.	194	7·64	0·0003	0·5	0·4

In 1895, the crops were, in cases 3 to 5, potatoes; 6 to 8, clover; 9 to 11, beet; 15, oats; 18 to 20, wheat, the other cases being the same as in 1896. No manure was applied.

The results of the experiments show, not only an enormous excess

in loss of nitrogen in the fallow cases as compared with the cases covered with vegetation, but that, supposing the whole of the nitrogen in the plants to have been taken up in the form of nitrates, the nitrogen of the crops and of the corresponding drainage may amount to less than that of the drainage from fallow land. In case 10, for instance, the total produce, straw and grain, is estimated to contain 61 kilograms of nitrogen per hectare (54·5 lbs. per acre), which, added to the nitrogen found in the drainage, makes 94 kilograms (84 lbs. per acre). In the fallow cases, the loss amounted to about 200 kilograms (180 lbs. per acre). This difference is ascribed to deficiency of rain in April and May, in consequence of which the soil bearing vegetation would become too dry for active nitrification, whilst the fallow soil would still retain sufficient moisture. When rain is abundant during the period of active vegetation, the nitrogen of the crop added to that lost in the drainage corresponds more nearly with the nitrogen lost in bare soil. This is illustrated by the results obtained with maize, which developed later; the total produce is estimated to contain 174 kilograms of nitrogen per hectare, which, when added to the loss in drainage, makes 197 kilograms.

The Grignon soil, when moist, is capable of yielding sufficient nitrates for the heaviest crops. By means of irrigation in the spring, increased nitrification could be induced and a great saving of nitrogenous manures effected.

Léon Martin (*ibid.*, 276—277) refers to the exceptionally wet winter, and the consequent loss of nitrates, which he supposes to be the cause of the unpromising appearance of the wheat crop (in May), and states that the power which straw has of retaining nutritive matters is of great value in wet seasons. He suggests that it would be of interest to ascertain the amount of nitrates lost by drainage in soils to which farmyard manure and mineral manures respectively had been applied.

Dehérain in reply (*ibid.*, 277—279), points out the importance of occupying the land as much as possible to avoid excessive drainage. It is doubtful whether the yellow appearance of the wheat was due to excess of water in the soil, experiments having shown that soil, during frequent rains, may contain less water after than before the showers. This is because the spaces between the particles of soil become less during rain. It is for this reason that the drainage through the cases is sometimes in excess of the rainfall.

Application of farmyard manure does not always render soil better able to retain water. At Grignon, soil thus manured gave slightly more drainage than the unmanured soil. N. H. J. M.

Analytical Chemistry.

Titration with Potassium Hydrogen Carbonate. By GEORGES FREYSS (*Chem. Centr.* 1896, ii, 511 ; from *Bull. Soc. Ind. Mulhouse*, **66**, 250—254).—This salt, being anhydrous and easily obtained in a

pure state, offers special advantages in volumetric analysis. A standard solution is made by dissolving 100 grams of the salt and making up to 1 litre.

To estimate the amount of caustic alkali in the presence of a carbonate, an excess of barium chloride is first added, and the standard solution is then run in until the red colour disappears, using phenolphthalein as indicator. To estimate bicarbonate in the presence of normal carbonate, a definite quantity of normal potash is first added, and the excess is then titrated as directed.

The solution may be used for determining the amount of alkali necessary to dissolve the phenols in tar-oil, or the phenolic compounds in essential oils. Normal soda is first prepared, using water previously saturated with phenols similar to those to be tested. Twenty grams of the tar-oil is agitated with 250 c.c. of the specially prepared normal soda, allowed to stand for a time, and then the aqueous layer is measured and drawn off. After clarifying with a little calcium carbonate, the liquid is filtered without delay, and in one-half of the filtrate the excess of alkali is titrated by simply adding normal potassium hydrogen carbonate until the liquid gets turbid. L. DE K.

Separation of Chlorine and Bromine in the Presence of Acetates, Sulphates, and Nitrates. By PAUL EHRHARDT JANNASCH and E. KÖLITZ (*Zeit. anorg. Chem.*, 1897, **15**, 66—67).—When the method for the direct separation of chlorine and bromine by means of potassium permanganate in strong acetic acid solution is employed, it is essential that acetates should not be present, as they retain the greater portion of the bromine. The presence of sulphates or nitrates is without influence on the reaction. Therefore, when the halogens are present in alkaline solutions, these must be neutralised or made faintly acid with sulphuric or nitric acid, but never with acetic acid. E. C. R.

Separation of Chlorine, Bromine, and Iodine in the Analysis of Organic Compounds. By PAUL EHRHARDT JANNASCH and E. KÖLITZ (*Zeit. anorg. Chem.*, 1897, **15**, 68—70).—The mixed halogens are obtained as silver salts either by Carius's method or by combustion of the organic compound with lime. The precipitate is then fused with pure sodium hydroxide in a silver crucible, the melt extracted with water, and the filtrate from the metallic silver, after being made slightly acid with sulphuric or nitric acid, is distilled with permanganate and acetic acid. E. C. R.

Estimation of Sulphur in Pig Iron. By ANDREW A. BLAIR (*J. Amer. Chem. Soc.*, 1897, **19**, 114—115).—The author and others find that there is a class of pig-irons in which the sulphur is evolved but incompletely as hydrogen sulphide when the sample is dissolved in hydrochloric acid, and that the residue is not oxidised by nitric acid, or even by aqua regia.

To estimate the total sulphur, Bamber's process is recommended. Five grams of the sample is dissolved in strong nitric acid; from 2 to 5 grams of nitre is added, the whole evaporated to dryness in a platinum dish, and the residue ignited. The product is then boiled with a weak

solution of sodium carbonate, and the sulphuric acid estimated in the filtrate with the usual precautions. L. DE K.

Estimation of Sulphur in Iron Pyrites or Native Zinc Sulphides. By A. NOAILLON (*Zeit. angw. Chem.*, 1897, 351—352).—The author has worked out a process by which all danger of losing sulphuric acid by evaporation is removed.

1·25 grams of the powdered material is treated with a mixture of 10 c.c. of nitric acid of sp. gr. 1·4, and 10 c.c. of a 30 per cent. solution of sodium chlorate; oxidation takes place rapidly in the cold. Excess of hydrochloric acid is then added, the mixture evaporated to dryness on a sand bath, the residue taken up with dilute hydrochloric acid, and the solution precipitated, while hot, with a slight excess of ammonia. When cold, the whole is made up to exactly 500 c.c. and then filtered. Two hundred c.c. of the filtrate, representing 0·5 gram of the sample, is then boiled to expel the ammonia, and after adding a slight excess of hydrochloric acid the sulphuric acid is estimated as barium sulphate.

L. DE K.

Estimation of Sulphur in Petroleum. By AUFRECHT (*Chem. Centr.*, 1896, ii, 361; from *Pharm. Zeit.*, **41**, 469).—Fifty c.c. of the sample is mixed with 0·5 gram of sodium hydrogen carbonate and submitted to distillation until only 5 c.c. is left in the retort. The residue is then transferred by means of ether to a large porcelain dish, and when the ether has volatilised another 0·5 gram of soda is added and the whole evaporated; finally, the residue is ignited with gradual addition of ammonium nitrate until the ash is quite white. The sulphuric acid derived from the sulphur in the sample is then estimated as usual. L. DE K.

Estimation of Sulphur in Coke. By N. OTEHA (*Zeit. angw. Chem.*, 1897, 330—331).—A quantity of the finely powdered material varying from 0·1 to 5 grams is boiled in a Wiborgh's apparatus with water, and some pieces of zinc or aluminium foil until all the air is expelled; hydrochloric or sulphuric acid is then introduced, and the boiling is continued for about 20 minutes. By this treatment, the sulphur is converted into hydrogen sulphide, which is carried off by the current of hydrogen; this is passed into a suitable absorbent such as bromine dissolved in hydrochloric acid so as to convert it into sulphuric acid, which is then estimated as usual, or it may be passed through a solution of cadmium acetate and estimated colorimetrically.

L. DE K.

Estimation of Nitrites and Nitrous Acid. By BRUNO GRÜTZNER (*Arch. Pharm.*, **235**, 241—245).—Nitrites may be estimated by adding potassium chlorate (free from chloride), excess of decinormal silver nitrate, and nitric acid, to the solution; the nitrous acid liberated decomposes the chloric acid with formation of nitric acid and hydrochloric acid, and the excess of silver is then titrated either with decinormal sodium chloride or decinormal ammonium thiocyanate. The difference between this and the amount of decinormal

silver originally added gives the hydrogen chloride formed, and consequently the nitrous acid originally present. J. F. T.

A New Reagent for Detecting and Estimating Nitrites. By M. C. SCHUYTEN (*Chem. Zeit.*, 1896, **20**, 722—723).—Antipyrin, which is so readily detected by means of nitrous acid, is, in turn, a valuable test for nitrites.

A 10 per cent. solution of antipyrin in acetic acid is made, and, when required, is diluted with water to ten times its bulk; 5 c.c. of this reagent is then added to 5 c.c. of the liquid under examination. Even when the amount of nitrous acid does not exceed 1 in 20,000, a permanent green coloration is noticed; the reaction is not interfered with by the presence of the heavy metals or of organic matter, but the colour at once changes to yellow if ferric salts or free hydrochloric or sulphuric acid is present.

The reaction may be utilised for the colorimetric estimation of nitrites in water, particularly as the presence of organic matters does not affect the reaction. A very weak standardised solution of a nitrite is used for comparison. L. DE K.

Estimation of Phosphoric Acid in Organic Substances. By C. GAROLA (*Chem. Centr.*, 1896, ii, 597; from *Rev. chim. anal. appliq.*, 1896, 269).—Estimation in the ash always gives low results. The author destroys the organic matter by heating with sulphuric acid as in Kjeldahl's process, neutralises with ammonia, acidifies with nitric acid, and precipitates the boiling solution with molybdate. The weight of the washed precipitate, after drying at 90°, when multiplied by 0·0354, gives the amount of P_2O_5. Solutions containing much silica are treated with ferric sulphate and precipitated by ammonia. The precipitate, after drying at 100—110°, is dissolved in nitric acid, the solution filtered from silica, and the phosphoric acid precipitated from the filtrate. M. J. S.

Estimation of Phosphoric Acid in Medicinal Wines. By F. GLASER and K. MÜHLE (*Chem. Zeit.*, 1896, **20**, 723).—One hundred c.c. of the sample is evaporated to a syrupy consistence in a 250 c.c. Kjeldahl flask, 25 c.c. of nitric acid is then added, and a gentle heat applied until an action is set up. When this has ceased, 75 c.c. more of the acid is added and the liquid is evaporated nearly to dryness over a small flame. When cold, 10 c.c. of sulphuric acid is added to the residue, also a drop of mercury, and the whole is boiled until colourless. The liquid is then diluted to the mark with water and 100 c.c. (equivalent to 40 grams of sample) is pipetted off, and after neutralising with ammonia the phosphoric acid is estimated by the citrate, or better still, by the molybdate process. L. DE K.

Detection of Arsenic. By DINKLER (*Chem. Centr.*, 1896, ii, 851; from *Pharm. Zeit.*, **41**, 638).—The author's method of employing Reinsch's test is to place a piece of clean copper foil in the mixture of the suspected matter with hydrochloric acid, and then to heat for

2 minutes very cautiously, so as to prevent the mixture from becoming brownish. Five minutes later, the foil is removed, dried, and heated in a tube in the usual manner. M. J. S.

Estimation of Boric Acid. By A. BELLOCQ (*Chem. Centr.*, 1896, ii, 563; from *Rev. intern. falsific.*, **9**, 119).—The following method, based on the solubility of boric acid in ether (0·8 gram in a litre) has been used in the analysis of the sulphuretted waters of Eaux Chaudes. The desulphuretted water is made alkaline and after being evaporated to dryness, the residue is incinerated, taken up with hydrochloric acid, and the excess of acid completely expelled at a moderate heat; the pulverised residue is then exhausted with ether in a separating bulb, and the ethereal extract evaporated over sulphuric acid in a desiccator. The residue is weighed and regarded as H_3BO_3. A qualitative test may be made by passing gaseous ammonia into the ethereal solution, which becomes turbid from formation of ammonium borate. M. J. S.

Estimation of Boric Acid. By SCHNEIDER and GAAB (*Chem. Centr.*, 1896, ii, 878; from *Pharm., Centr. H.*, **37**, 672—673).—Boric acid volatilises so readily with absolute alcohol, that a 0·5 per cent. solution leaves scarcely any residue on distillation. To examine flesh for boric acid, the finely divided substance is heated in a covered beaker on the water bath, powdered when cold, and rubbed with anhydrous sodium sulphate to absorb the water; it is then extracted with boiling absolute alcohol, and the filtered extract distilled. The distillate is mixed with soda, evaporated, and the boric acid estimated by known methods.
M. J. S.

Estimation of Boric Acid in Foods. By LEONARD DE KONINGH (*J. Amer. Chem. Soc.*, 1897, **19**, 55—56).—The process recommended applies to raw yolk of egg and also to milk. The sample, after being rendered alkaline with sodium hydroxide, is incinerated, the ash is boiled with water, and the alkaline filtrate rendered distinctly acid to methyl-orange by means of weak sulphuric acid. After boiling to expel any carbonic anhydride, the liquid is cooled and mixed with half its bulk of glycerol. The boric acid is then titrated with decinormal soda, using phenolphthalein as indicator (Thomson's process). On account of the presence of soluble phosphoric acid, the titration will be somewhat in excess of the truth, but a correction for this may be made by allowing 3 c.c. of soda when operating on 5 grams of yolk of egg, or 1 c.c. when operating on 10 grams of milk. When the acid is present, in large and consequently harmful quantities, the results are sufficiently accurate. L. DE K.

Estimation of Boric Acid as Potassium Borofluoride. By KONSTANTIN THADDÉEFF (*Zeit. anal. Chem.*, 1897, **36**, 568—637).—The accurate estimation of boric acid has long been recognised as one of the most difficult analytical operations; Rose and others confined their methods to the estimation of the bases, and calculated the boric acid from the deficiency. The author, being desirous of analysing a specimen of the rare mineral, sulfoborite (a double magnesium borate and sulphate), obtained from the residues of carnallite solutions,

previous analyses, when boric acid was estimated by difference, having shown a deviation of 1·88 per cent. from the theoretical proportion, made a preliminary study of the methods proposed for the estimation of boric acid; these are reviewed at considerable length, and their weak points indicated. By analyses of a specimen of pure crystallised borax, he shows how unsafe it is to trust to a differential method, even in so simple a case. A modification of the Berzelius-Stromeyer method, when performed exactly according to the following description, affords unexceptionable results. Since the method requires the absence of all bases except potassium, it is necessary, when dealing with borates, to employ Rosenbladt's method of distillation with sulphuric acid and methylic alcohol, which, according to Rieschle, is more exact than that proposed by Gooch (Abstr., 1887, 299). Rosenbladt's apparatus is, however, simplified; a flask is fitted with a tube for the admission of purified air, a stopcock thistle funnel with safety bend, and a long delivery tube dipping into a solution of potassium hydroxide in a platinum basin. It is best to mix the sulphuric acid (2—3 c.c.) with 10 c.c. of methylic alcohol in a separate vessel, and introduce it through the funnel after cooling. The air supply, which is controllable by a stopcock, assists greatly in maintaining the regularity of the distillation. For quantities of boric acid (H_3BO_3) up to 1 gram, 2 grams of the purest potash (80 per cent. of KHO) in 200 c.c. of water is placed in the basin. After four quantities of methylic alcohol (10 c.c. each) have been distilled over, the contents of the basin are concentrated to one-half on the water bath, an excess of pure hydrofluoric acid is then added, and the evaporation continued until the odour of hydrofluoric acid has almost disappeared. After cooling, 50 c.c. of a clear solution of potassium acetate of 1·14 sp. gr. is added, and the contents of the basin are frequently stirred during 2 hours with a platinum rod, to effect the solution of the potassium hydrogen fluoride; warming at this stage must be avoided. 100 c.c. of alcohol (sp. gr. 0·805) is then added, and after thorough stirring, the whole is left for 12—14 hours. Meanwhile the filter is prepared; a Schleicher and Schull, No. 590, 9 cm. in diameter, is moistened with alcohol (which is found to increase its dry weight by 1—2 miligrams), dried at 100—110° for 2—3 hours, and weighed in a well-fitting stoppered tube. The undissolved residue of potassium borofluoride is transferred from the basin to the filter by rinsing with alcohol of 0·805 sp. gr., with which also it is further washed until a drop of the filtrate leaves no more residue on platinum foil than would be left by an alcoholic solution of the borofluoride (0·000014 gram per c.c.). On account of this solubility, the amount of alcohol should be restricted as much as possible; 60—70 c.c. usually suffices, and the washing is much facilitated by tapping and shaking the funnel; the filter and precipitate are dried for 3 hours as above and weighed. The success of the method depends on the fact that the special mixture of acetate and alcohol is capable of retaining potassium hydrogen fluoride in solution, and that the mixture of the three substances, in the proportions resulting from the use of 2 grams of potash, has an extremely feeble solvent action on the potassium borofluoride. The weighed precipitate should be tested for fluorides by boiling with water and adding calcium chloride to the

cold filtered extract. Out of seven analyses of borax by the above method, only two deviated more than 0·07 per cent. from the theoretical proportion of B_2O_3. M. J. S.

Rapid Method for Estimating Silicon in Silicospiegel and Ferrosilicon. By C. B. MURRAY and G. P. MAURY (*J. Amer. Chem. Soc.*, 1897, **19**, 138—139).—0·5 gram of the finely divided sample is placed in a dish, 50 c.c. of water, 10 c.c. of hydrochloric acid (sp. gr. 1·2) and 12 c.c. of dilute sulphuric acid (1 : 3) are added and the whole evaporated until copious fumes of sulphuric acid are given off. When cool, 10 c.c. of hydrochloric acid is added and then 70 c.c. of water. On boiling, no effervescence should be noticed; if any occurs, the liquid must again be evaporated until sulphuric acid fumes make their appearance. The undissolved residue is collected, thoroughly washed with dilute hydrochloric acid (1 : 1) and hot water, ignited in a platinum crucible, and weighed. A few drops of sulphuric acid are added to the weighed residue, then enough hydrofluoric acid to dissolve the silica, the whole is evaporated, and the residue ignited to decompose the sulphates; the loss in weight equals the silica, which is then calculated to silicon. It is stated that an analysis may be finished in 30 minutes.

L. DE K.

Electrolytic Examination of Silicates. By MAYENÇON (*Chem. Centr.*, 1896, ii, 925; from *Ind. minérale*; *Berg.-Hüttenm. Zeit.*, **55**, 333).—The most insoluble silicates are decomposed by electrolysis if powdered and made into a paste with water, the silicic acid passing to the positive and the other elements to the negative electrode. The silicate paste should be placed on a metal plate connected with the negative pole, and covered with a piece of filter paper upon which the positive plate is laid. If the latter consists of silver, zinc, or copper, silicates of these metals are formed. M. J. S.

Limits of Delicacy of Various Tests for Metals. By B. NEUMANN (*Chem. Zeit.*, 1896, **20**, 763—764).—The author has compiled an exhaustive table showing the highest degree of dilution in which a reaction is still visible with the tests for the more important metals. The names of the various observers are given, the author himself being responsible for 62 of the statements. L. DE K.

Estimation of Alkalis in Fire-Clays. By CARL REINHARDT (*Chem. Centr.*, 1896, ii, 265—266; from *Stahl. ü. Eisen.*, **16**, 448—452).—After the sample has been treated with hydrofluoric and sulphuric acids to remove the silica, the residue is dissolved in boiling water, and the solution made alkaline with ammonia, using rosolic acid as indicator; hydrogen peroxide is then added to complete the precipitation of the alumina, oxide of iron, &c. After making up to a definite bulk, two-thirds of the liquid is filtered, evaporated to dryness, and carefully ignited; the residue is then again treated with a few drops of the acid mixture, and, after ignition, boiled with a little hydrochloric acid. After diluting with water, the lime is precipitated by ammonia and ammonium oxalate, the filtrate evaporated to dryness, and the residue ignited to expel the ammoniacal salts. The residue is then taken up with water, and the clear solution mixed with excess of sulphuric

acid; this, on evaporation, leaves the magnesia, potash, and soda as sulphates. After strongly heating with addition of some solid ammonium carbonate, the mixed sulphates are weighed, and then dissolved in a measured quantity of water. In one half of the liquid the magnesia is estimated, in the other half the sulphuric anhydride, the alkalis thus being obtained by difference.

The author advises making a blank experiment, so as to allow for any traces of alkalis in the reagents. L. DE K.

Direct Estimation of Calcium Carbonate in Soil. By FAUSTO SESTINI (*Ann. Agron.*, 1897, **23**, 326—327).—The soil (5 grams) is boiled for an hour with 1 per cent. acetic acid (100 c.c.) in a reflux apparatus, allowed to cool, and filtered through a dry filter paper; 55 c.c. of the filtrate is evaporated to 5 c.c., treated with hydrochloric acid (sp. gr. = 1·1), and evaporated until all the acetic acid has disappeared. The residue is then dissolved in a little water, and ammoniacal solution of ammonium chloride (10 c.c.) added, after which the volume of the liquid is made up to 55 c.c. with 75 per cent. alcohol. The precipitate (calcium sulphate and ferric oxide) is separated by filtration, and 50 c.c. of the filtrate (corresponding with 2·5 grams of soil) precipitated with ammonium oxalate. N. H. J. M.

Estimation of Zinc by Electrolysis. By EDUARD JORDIS (*Chem. Centr.*, 1896, ii, 449—450; from *Zeit. Elektrotech. ü. Elektrochem.*, **2**, 655—657).—Platinum dishes may be quickly coated with copper by using a cold saturated solution of copper sulphate mixed with 5 per cent. of nitric acid; at a temperature of 50—60° and with a current of 1—1·5 ampère, the operation is finished in 2 minutes. The zinc solution, measuring from 120—150 c.c. and containing from 0·3—0·5 gram of metal, is mixed with 2 grams of ammonium sulphate, 5—7 grams of ammonium lactate, and a few drops of lactic acid, and introduced into a copper-coated platinum dish. To prevent the oxidation of the zinc, the dishes should not be filled too full, so as to leave a few mm. of copper deposit above the surface of the liquid. When, after 40 minutes, the bulk of the metal has been deposited, using a current of 1—1·5 ampère, the liquid is poured into a second platinum dish and the electrolysis continued for another 20—25 minutes.

When a speedy result is desired, the electrolysis may be conducted at the boiling temperature; in this case, the liquid must be kept from getting too acid by cautiously adding ammonia. L. DE K.

Contributions to Qualitative Analysis. By ALVAREZ and JEAN (*Chem. Centr.*, 1896, ii, 513—514; from *Répert. Pharm.*, 1895, 440).—*Detection of Zinc, Chromium, Manganese, and Iron.*—The solution is boiled with excess of aqueous potash, filtered, and the filtrate tested for zinc by means of sodium sulphide. The potash precipitate is then boiled with aqueous potash and excess of lead dioxide; if chromium is present, a yellow solution is obtained from which lead chromate is thrown down on adding acetic acid. The undissolved lead dioxide, when boiled with nitric acid, gives a violet coloured solution if manganese is present. The iron is then tested for by pouring off the nitric acid, dissolving the residue in hydrochloric acid, and adding potassium thiocyanate.

Detection of Alkali Sulphides, Thiosulphates, and Sulphites.—Sulphides are tested for by sodium nitroprusside, which gives a violet coloration. A portion of the solution is mixed with an ammoniacal solution of zinc oxide, heated to expel the ammonia, filtered, and the filtrate tested for sulphite and thiosulphate by adding, first 6 times its bulk of 95 per cent. alcohol, and then, cautiously, a solution of bismuth subnitrate in nitric acid. The presence of thiosulphate is indicated by a dense, yellowish-brown precipitate of bismuth thiosulphate; this is allowed to subside, and then more of the reagent is added, when a white precipitate is formed if a sulphite is present. The presence of a sulphite may also be detected by means of iodic acid, starch solution, and acetic acid.

Detection of Chlorides, Chlorates, and Nitrates.—After removing the whole of the chloride by silver acetate, acetic acid and zinc are added to the filtrate and the whole is warmed; a further precipitate of silver chloride is first formed if a chlorate is present, but this is gradually reduced to metallic silver. The zinc and acetic acid convert the nitric acid into ammonia, which may be detected by means of Nessler's reagent. L. DE K.

Estimation of Mercuric Salts. By LUDWIG VANINO and F. TREUBERT (*Ber.*, 1897, **30**, 1999—2001).—To the solution of mercuric salt (containing about 0·5 gram Hg per 100 c.c.), hydrogen peroxide is first added, and then, gradually, commercial hypophosphorous acid (of sp. gr. 1·15) in slight excess; the precipitate of mercurous chloride is washed with cold water, collected on a tared filter, dried at 100°, and weighed. The presence of hydrogen peroxide prevents a further reduction of the mercurous chloride to mercury, which otherwise takes place. In 8 experiments with mercuric chloride, the percentage of Hg as found varied from 73·80 to 73·99, the calculated percentage being 73·80. C. F. B.

Improvements in the Colorimetric Test for Copper. By GEORGE L. HEATH (*J. Amer. Chem. Soc.*, 1897, **19**, 24—31).—The following process is recommended. 2·5 grams of the material, lean blast-furnace slags, for example, is heated in a porcelain dish with 15 c.c. of nitric acid, and after adding 5 c.c. of sulphuric acid the evaporation is continued until the mass has become a thick, but rather soft, paste; it is then treated with 70 c.c. of water to dissolve the copper sulphate, and 30 c.c. of ammonia is added. The liquid is filtered, and the residue after being twice washed with 10 c.c. of dilute ammonia (1 : 10), is rinsed back into the dish, using 50 c.c. of water, taking care not to damage the filter, and enough sulphuric acid is added to redissolve the iron and alumina; 25 c.c. of ammonia is again added, and the filtrate and ammoniacal washings are mixed with the main filtrate, which is then transferred to a tall cylinder of thin, colourless glass, and made up with dilute ammonia to 200 c.c. The colour of the liquid is compared with those of a series of copper solutions of known strength contained in similar cylinders; these standard solutions keep very well if the copper is present as sulphate and the liquid contains a large excess of ammonia, provided they are kept from the light in a cool place. L. DE K.

Estimation of Copper in Vegetable Foods. By VICTOR VEDRÖDI (*Chem. Zeit.*, 1896, **20**, 584—585).—The author recommends eliminating any soluble silicic acid and also the oxide of iron from the ash of vegetable foods when testing the same for copper. If this precaution be not taken, the precipitate which always forms on adding ammonia to the acid solution of the ash will carry down with it a not inconsiderable amount of copper, and the filtrate will be deficient in colour.

Instead of burning the sample, it may also be "mineralised" by heating first with nitric acid and then with strong sulphuric acid.

L. DE K.

Analysis of Aluminium and its Alloys. By HENRI MOISSAN (*Compt. rend.*, 1897, **125**, 276—278).—The residue left when aluminium is treated with dilute hydrochloric acid (20 : 100) contains at least 10 per cent. of iron, and does not consist only of carbon, copper and silicon, as Balland has stated (*Compt. rend.*, **124**, 1311); on the other hand some of the copper is dissolved even when a more dilute acid (10 : 100) is used. Further, when the aluminium is treated with hydrochloric acid (10 : 100) to which a small quantity of nitric acid is added, the residue does not consist of carbon and silicon only, as Balland stated, but contains a large proportion of iron and about 10 per cent. of copper.

Some recent specimens of aluminium were found to contain 99·21 to 99·61 per cent. of that metal, with 0·41—0·54 per cent. of iron, 0·05—0·11 of silicon, 0·00—0·02 of sodium, and traces of copper.

C. H. B.

Detection of Alum in Flour and Bread. By JOSEF VAN DER PLANCKEN (*Chem. Centr.*, 1896, ii, 563; from *Ann. Pharm. Louvain*, 1896, May).—The test with campeachy wood tincture succeeds only with fresh flour, and fails with sour bread. From 10 to 20 grams of flour or powdered bread is made into a paste with water, some sodium chloride (free from carbonate) is added, then 10 drops of fresh logwood tincture and 5 grams of calcium carbonate, and the whole is made up to 100 c.c. The clear, supernatant liquid will exhibit a bluish-grey coloration in presence of 0·1 per cent. of alum; in the absence of alum, the liquid is reddish-violet.

M. J. S.

Estimation of Calcium, Aluminium, and Iron in Mineral Phosphates. By LEON LINDET (*Compt. rend.*, 1897, **125**, 246—247).—In the ordinary method for the analysis of mineral phosphates, the phosphoric acid is precipitated by magnesia mixture in presence of a large quantity of ammonium citrate, and the destruction of this salt for the purpose of estimating iron, &c., is troublesome and tedious. Citric acid and citrates can, however, readily be oxidised by means of the reaction described by Villiers (this vol., ii, 492). The solution is acidified with nitric acid, 0·5 gram of manganese sulphate or nitrate added, and then 50 c.c. of concentrated nitric acid for every 20 grams of citric acid present; the liquid is carefully heated, and more nitric acid is added from time to time until there is no further evolution of gas. The metals are afterwards separated in the usual way.

Vanadyl dichloride acts much more energetically than manganese salts, and 0·1 gram will readily bring about the oxidation of 20 grams of citric acid. As ammonium hypovanadate is insoluble in excess of ammonia, it is precipitated with the ferric and aluminium hydroxides, and the weight of the vanadium oxide must be subtracted from the weight of the mixed oxides which are left after strongly heating. It is convenient to use a 1 per cent. solution of vanadyl dichloride, the strength of which is checked by precipitating 10 c.c. of the solution with ammonia in presence of a known quantity of a ferric salt, and weighing the precipitate after strongly heating.

In either case, the calcium is estimated in the usual way in the liquid from which aluminium, iron, and manganese or vanadium have been removed. C. H. B.

Detection of Nickel in Presence of Cobalt. By ANSELMO CAVALLI (*Gazzetta*, 1897, **27**, ii, 95—96).—In the group precipitate, the author extracts the zinc and manganese sulphides from those of cobalt and nickel by dilute hydrochloric acid (1 : 5) and after washing the residue with very dilute ammonium sulphide, dissolves it in nitro-hydrochloric acid, evaporates to dryness, and adds a little water; on treating the solution with sodium nitroprusside, both nickel and cobalt are precipitated, although only slowly from dilute solutions. The nickel compound is dissolved on treating this precipitate with dilute ammonia, but not the cobalt. W. J. P.

Complete Analysis of Iron Ores: Notes on Särnström's Method of Estimating Manganese. By GEORGE AUCHY (*J. Amer. Chem. Soc.*, 1897, **19**, 139—153).—When using Särnström's process for estimating manganese in presence of iron, it is necessary to be very careful not to add any excess of sodium carbonate before titrating with potassium permanganate, as otherwise the precipitated ferric oxide may carry down a small proportion of the manganese; the author states that this danger is greatly lessened if about 7 grams of ammonium chloride is added before the soda.

A process for the full analysis of iron ores is given, of which the following is an outline. The ore is dissolved in hydrochloric acid, the siliceous matter separated by evaporation, the residue treated with acid, and the filtrate largely diluted. After adding a sufficiency of ammonium chloride, the excess of acid is first neutralised with solid sodium carbonate, and then a solution of the latter is added until a precipitate begins to form; on boiling, the bulk of the iron is precipitated, and the last traces are thrown down on adding a few more drops of soda solution. The filtrate, after being heated to boiling, is mixed with ammonia to precipitate the alumina, filtered, and the manganese in the filtrate titrated with permanganate. The liquid, which may contain calcium and magnesium, after removal of all the manganese as sulphide, may be analysed in the usual manner.

The alumina precipitate is dissolved in hydrochloric acid; the ferric precipitate also and the two solutions are united; the iron and aluminium are now precipitated by ammonia, and the filtrate, which may contain calcium and magnesium, may be advantageously united with the main calcium and magnesium solution. The oxides of iron and

aluminium, after having been weighed together, are dissolved, and the iron is estimated volumetrically. L. DE K.

Estimation of Tin in Tin Plate. By HUGO MASTBAUM (*Zeit. angw. Chem.*, 1897, 329—330).—Twenty-five grams of the material, cut up into small pieces, is boiled with 50 c.c. of hydrochloric acid containing 10 per cent. of HCl. The tin coating soon dissolves, and the solution is at once poured off and diluted to 250 c.c.; 50 c.c. of it is then introduced into a 100 c.c. flask, neutralised with ammonia, and mixed with 10 c.c. of yellow ammonium sulphide. Water is now added up to the mark, the mixture filtered, and 50 c.c. is pipetted off and acidified with acetic acid to precipitate the stannic sulphide.

When completely settled, the precipitate is collected on a filter and washed with a 10 per cent. solution of ammonium acetate. The sulphide is converted into stannic oxide in the usual manner by roasting and final ignition with addition of a lump of ammonium carbonate.

L. DE K.

Action of Hydrogen Peroxide on Metals as Precipitated by Hypophosphorous Acid: Detection of Arsenic, Antimony, and Bismuth in the Presence of the Noble Metals. By LUDWIG VANINO (*Ber.*, 1897, **30**, 2001—2003).—The metals are precipitated by warming the acid solution with hypophosphorous acid; gold, silver, and mercury are even precipitated in the cold (platinum, iridium, and rhodium are not precipitated at all). The arsenic, antimony, and bismuth (also copper) in this precipitate can be dissolved by means of hydrogen peroxide, and their presence demonstrated by warming the solution with hypophosphorous acid; gold, silver, mercury, ruthenium, palladium, and osmium are not dissolved. C. F. B.

Apparatus for Testing Oils. By A. GAWALOWSKI and ALEXANDER KATZ (*Chem. Centr.*, 1896, ii, 451; from *Centr. Nahr. ü. Genussm. ü. Hyg.*, **2**, 213—214).—When testing fatty or mineral oils, or a mixture of the same, it is advisable to determine the coefficient of solubility in alcohol and ether as proposed by Gawalowski. For this purpose, 2·5 grams of the sample is dissolved in 10 c.c. of ether slightly coloured with "alkannin 1," 4 c.c. of this solution is placed in a specially constructed apparatus, and 95 per cent. alcohol is gradually added from the burette which forms part of the apparatus, until the liquid turns red and turbid, so that the printed lines of the paper on which the apparatus is placed are no longer visible. Suppose 10·2 c.c. of alcohol are required, the degree of coefficient of solubility will be 10·2. Different samples of oil give very different figures.

The apparatus is so constructed that no perceptible evaporation of ether can take place during the titration. L. DE K.

Analysis of Essence of Lemons. By ARTURO SOLDAINI and E. BERTÉ (*Gazzetta*, 1897, **27**, ii, 25—34).—The authors' method for detecting the adulteration of lemon oil (*Sull' analisi dell' essenza di limone*, Messina, 1896) having been recently criticised (*Schimmel's Report*, April, 1897, 19), the authors quote more analytical data, and state that adulteration can always be detected by their method, although the quantity of foreign oil added may not be always ascertainable.

Although citral cannot be accurately determined in lemon oil, yet, if it could, the determination would hardly help in detecting adulteration, the proportion of citral in genuine lemon oil being very variable.

Lemon oil is genuine if, after distilling off one-half of the sample, the distillate has a higher rotation than, and the residue a rotation lower than, or equal to, that of the original oil; the difference must be at least 0° 30'. If 2 per cent. of turpentine is added, this difference disappears, and the addition of a larger quantity causes the difference to be of opposite sign. W. J. P.

Analysis of Coals. By FRITZ HABER and S. GRINBERG (*Zeit. anal. Chem.*, 1897, **36**, 557—567).—The valuation of the calorific power of a coal by estimating the carbon and hydrogen has hitherto presented difficulties, due mainly to the fact that methane is burnt by copper oxide only at a temperature high enough to soften combustion tubing. The authors obviate this difficulty by the use of platinised asbestos, which effects the combustion of methane in oxygen at 414°. The combustion tube, 430 mm. in length, is charged as follows: 30 mm. are left empty; then comes a plug of copper gauze 10 mm. in length; after this 60 mm. of granular lead chromate, a 5 mm. plug of copper gauze, next 1 gram of 10—20 per cent. platinised asbestos teased out so as to occupy 100 mm. of the tube, and finally a gauze plug 5 mm. long. The remainder is left empty to receive the boat containing the coal, and so much of the tube as is occupied by the above materials, as well as a sufficient length to include the boat, but not the whole tube, is wrapped in stout copper gauze. To the empty end of the tube is attached the usual absorbing apparatus, whilst to the other is fitted a T-piece, through the horizontal limb of which a wire (stout copper with a platinum end) can be worked backwards and forwards in its caoutchouc stopper. The platinum wire is hooked, and serves either to push the boat forward or pull it back. The tube is heated by two Teclu burners. The boat, containing about 0·25 gram of coal, is placed in the uncovered part of the tube, purified oxygen is admitted by the side limb of the T-piece at the rate of 2—3 bubbles per second, and the boat is then slowly pushed forward (about 10 mm. every 10 minutes) into the heated region until it touches the copper plug. In this way, any moisture it contains is first driven off, and the expulsion of the volatile hydrocarbons then takes place gradually. The coke should burn with a red glow; if it glows with a yellow light, the oxygen stream and the whole combustion are too rapid. A single tube suffices for 8—10 analyses, and excellent results are obtained with coals of widely varying composition. No provision being made for the reduction of nitrogen oxides, traces of nitrous and nitric acids are found in the absorbing apparatus, but their amount is too small to be of technical importance; it is stated that sulphuric acid is not found.

M. J. S.

Estimation of Alcohol in Essences. By RUDOLF HEFELMANN (*Chem. Centr.*, 1896, ii, 932—933; from *Pharm. Centr.-H.*, **37**, 683).—The official method consists in diluting with about 2 volumes of water and mechanically precipitating the ethers by addition of solid sodium chloride, then distilling out the alcohol from the sodium chloride

solution. The method does not give satisfactory results with eau de Cologne. From essences diluted until the alcohol amounts to 40—60 grams per 100 c.c., the ethers and aromatic oils can be removed by shaking with light petroleum (sp. gr. = 0·64—0·67; boiling point 55—75°); 25 c.c. of essence is therefore diluted with an appropriate volume of water, shaken in a separator bulb with 50 c.c. of light petroleum, and after 3—5 hours' repose the clear lower layer is run off, and a measured volume of it, further diluted with half its volume of water, is distilled. The alcohol in the distillate is ascertained by taking the specific gravity in the usual manner. All the liquids should be at 15° when measured. M. J. S.

New Reaction of Picric Acid. By A. SWOBODA (*Chem. Centr.* 1896, ii, 717; from *Z. Oesterr. Apoth.-V.*, **34**, 617).—On treating a cold aqueous solution of picric acid with a cold aqueous solution of methylene-blue, there is immediately produced a violet, flocculent precipitate, soluble with blue or green colour in ether, chloroform, or hot water. The chloroform solution leaves a blue residue when evaporated. Lacquers coloured with picric acid are first dissolved with a little alcohol. M. J. S.

Improvements in Paper Testing. By SIEGMUND FERENCZI (*Zeit. angw. Chem.*, 1897, 436—441).—The sample is examined microscopically; this investigation being much assisted by using appropriate staining materials such as a solution of malachite-green acidified with acetic acid, or a weak alcoholic solution of rosaniline sulphate containing excess of sulphuric acid. If excess of incrustating matter such as lignin or lignose is found, the paper cannot be considered as likely to be very durable.

In order to test the capacity of a sample of paper to resist crumpling, the author prefers using either the apparatus devised by Pfuhl or the one invented by Schopper. For details of these complicated pieces of apparatus, the original paper should be consulted. L. DE K.

New Method of Detecting Formaldehyde. By LEBBIN (*Chem. Centr.*, 1896, ii, 930; from *Pharm. Zeit.*, **41**, 681).—A few c.c. of a formaldehyde solution mixed with about 0·05 gram of resorcinol, and then with about its own volume of 50 per cent. soda solution, when boiled, develops a rich, permanent red coloration. The reaction is not given by other aldehydes. It will detect 1 part of formaldehyde in 10 million of water. M. J. S.

Estimation of Aldehyde in Alcoholic Liquids. By E. RIETER (*Chem. Centr.*, 1896, ii, 368; from *Schweitz. Wochs. Pharm.*, **34**, 237—239).—When dealing with a colourless liquid, 5 c.c. of 0·05 per cent. sulphurous acid is put into a 100 c.c. flask together with 20 c.c. of the liquid to be tested, which should not contain more than 0·0025 per cent. of aldehyde; after making up to the mark with water and thoroughly mixing, it is put aside for 4 hours. Fifty c.c. of the mixture is taken out, and the free sulphurous acid is titrated, as usual, with N/200, or, if more aldehyde was present and consequently more sulphurous acid entered into combination, with N/100 iodine. The remainder of the liquid is mixed with 25 c.c. of normal potash

which rapidly decomposes the compound and the total sulphurous acid is then titrated as before, after adding a sufficiency of dilute sulphuric acid. The difference between the two titrations represents the amount of sulphurous acid combined with the aldehyde.

Coloured alcoholic liquors are first diluted with water and then submitted to distillation, the colourless distillate being treated as described above. L. DE K.

Estimation of Hydrocyanic Acid in Oil of Bitter Almonds. By EDWARD KREMERS and O. S. SCHREINER (*Chem. Centr.*, 1896, ii, 928; from *Pharm. Review*, 1896, Sept.).—Silver nitrate is added to an aqueous solution of the oil, then excess of ammonia, and immediately afterwards nitric acid. The object of the ammonia is to decompose the benzalcyanhydrin, in which most of the cyanogen of the oil is contained, and from which it cannot be directly precipitated by silver nitrate. The hydrocyanic acid may be titrated with silver nitrate (using chromate as indicator) if the oil is mixed with a paste of magnesium hydroxide. M. J. S.

Estimation of Volatile Fatty Acids by the Leffmann-Beam Process. By W. KARSCH (*Chem. Zeit.*, 1896, **20**, 607—608).—The author recommends this process for the analysis of butter, as it dispenses with the use of alcohol and so prevents the results being vitiated by the absorption of carbonic anhydride during the evaporation.

This process, as will be remembered, consists in saponifying the butter with a solution of sodium hydroxide in glycerol. L. DE K.

Detection of Lactic Acid and its Clinical Significance. By J. H. DE JONG (*Chem. Centr.*, 1896, ii, 806—807; from *Arch. f. Verdauungskrankh.*, **2**, Part I.).—To detect free lactic acid in the gastric juice by Uffelmann's test, 5 c.c. of the gastric juice mixed with 1—2 drops of hydrochloric acid is cautiously evaporated to a syrupy consistence and extracted with a little ether. The ethereal solution is added drop by drop to 5 c.c. of boiling water in a test-tube, and when the ether has evaporated and the water cooled, a drop of a 5 per cent. solution of ferric chloride is added. The colour is then compared with that produced in a standard solution of lactic acid. For clinical purposes, Nessler's test is too sensitive; Boas' method (*Chem. Centr.*, 1894, i, 338; ii, 334) is more suitable. Regard should be paid to the combined as well as the free lactic acid. The ethereal extract obtained from 20 c.c. of gastric juice by Boas' process is heated in a flask with manganese dioxide and sulphuric acid, and the aldehyde produced is collected in a bottle connected air tight with the Liebig's condenser, charged with 20 c.c. of water and plunged in ice. The stopper of the bottle is furnished with a second tube, which also passes through the condenser jacket and serves for the escape of air without loss of aldehyde. After distilling over three-quarters of the solution and aspirating air through the apparatus, an excess (20 c.c.) of N/10 iodine solution and 20 c.c. of pure soda are added, and after a few minutes the clear liquid is acidified and the amount of iodine not consumed in forming iodoform is titrated by thiosulphate. Healthy gastric juice contains

only traces of lactic acid. Larger amounts may be formed in cases where secretion and peristaltic action are both deficient, but in the absence of gastric carcinoma its formation is exceptional; in the presence of carcinoma, it occurs almost invariably. M. J. S.

Detection of Calcium Hydrogen Tartrate in Purified Cream of Tartar. By HENRIK ENELL (*Chem. Centr.*, 1896, ii, 515; from *Nordisk. Farm. Tidskr.*, 11, 393).—One gram of the sample is charred, the residue extracted with very dilute hydrochloric acid, and the filtered solution mixed with excess of ammonia and ammonium oxalate; the precipitated calcium oxalate is then treated in the well-known way with standard potassium permanganate. L. DE K.

Estimation of Uric Acid in Guano. By ALBERT STUTZER and A. KARLOWA (*Chem. Zeit.*, 1896, **20**, 721—722).—About two grams of the sample is treated with water feebly acidified with hydrochloric acid, the whole evaporated to dryness, and the residue taken up with 100 c.c. of water in which 3 grams of piperazine has been dissolved; the mixture is then boiled for 1 minute, filtered, coloured with a drop of phenolphthalein solution, and after sufficient hydrochloric acid has been added to destroy the alkaline reaction, 10 c.c. more of 10 per cent. hydrochloric acid is added; the whole is then well stirred and left for 12 hours. The crystallised uric acid which separates is collected on a very small filter, washed with water containing 1 per cent. of hydrochloric acid until the total filtrate measures 200 c.c., after which the filter and its contents are treated by the Kjeldahl process. The amount of nitrogen found, multiplied by 3, gives the uric acid originally present in the guano. As, however, uric acid is not absolutely insoluble in water, a slight correction must be made; the authors advise adding 0·003 gram to the quantity of uric acid found. L. DE K.

Estimation of Salicylic Acid. By FRANZ FREYER (*Chem. Zeit.*, 1896, **20**, 820—821).—The author states that salicylic acid may be estimated in the same way as phenol by means of bromine. The solution is treated with a mixture of potassium bromate and potassium bromide; dilute hydrochloric acid is added, and then after about 4 minutes, excess of potassium iodide solution. The liberated iodine is titrated by means of approximately N/10 sodium thiosulphate, a blank experiment being, of course, made, and the difference in the amount of thiosulphate noted. The process cannot be used for estimating this acid in beer or wine, unless the acid has been previously isolated by the use of ether and light petroleum. To test qualitatively for the acid, the author recommends distilling the beer or wine, when the acid will be found chiefly in the last fractions of the distillate; the ferric chloride test may then be applied. Hoorn's statement that beer when distilled yields a substance giving a violet coloration with ferric chloride has not been confirmed by the author. L. DE K.

Estimation of Kynurenic Acid. By ACHILLE CAPALDI (*Zeit. physiol. Chem.*, 1897, **23**, 92—98).—Although the methods described by Schmiedeberg and Schultzen (*Annalen*, 1872, **164**, 155) and by

Jaffé for the estimation of kynurenic acid in urine give fairly satisfactory results, they are to be objected to on account of the time which they take, and also because the kynurenic acid obtained is always mixed with colouring matter, which cannot easily be got rid of without loss of material.

The author suggests the following method by which the kynurenic acid is obtained perfectly pure.

The urine is mixed with half its bulk of a 10 per cent. solution of barium chloride containing 5 per cent. of concentrated ammonium hydroxide, evaporated to one-third of the volume of urine taken and acidified with concentrated hydrochloric acid. The precipitated kynurenic acid is filtered, dissolved in aqueous ammonia, reprecipitated, and weighed. A. W. C.

The Critical Temperature of Liquids and a New Method for Identifying Fats and Oils. By ALEXANDER VON ASBÓTH (*Chem. Zeit.*, 1896, **20**, 685—686).—The author confirms the results obtained by Crismer, who found that there is a great difference between the critical temperature of butter and margarine. The investigation will be continued. (Compare Abstr., 1896, ii, 506.) L. DE K.

Use of the Iodine Number in the Analysis of Wool Fat. By W. HERZIG (*Chem. Centr.*, 1896, ii, 936; from *Ding. Poly. Journ.*, **302**, 17).—The author has already shown that the iodine number can be employed in forming an opinion on a wool fat. He has now examined the iodine absorption of the various groups into which a specimen of wool fat can be separated, with the object of ascertaining the amount of the unsaturated substances in each group, and of employing the iodine absorption of the separated groups as an analytical method. The conclusions arrived at from the examination of a single sample, obtained from a South American wool, by extraction with ether, are as follows. Besides fatty acids, only unsaturated substances exhibiting the same iodine number as cholesterol are present; the presence of isocholesterol is also very probable. Saturated higher alcohols cannot be present, since those in wool fat are readily soluble in organic menstrua, whilst cerylic alcohol is sparingly soluble, and the absence of any considerable amount of such substances is further indicated by the iodine number. The results show that where saponification under pressure is necessary, that operation can be resorted to without more intimate decomposition. After removal of the free fatty acids, the fatty acids obtained by saponification show a very low iodine absorption, and therefore contain a very small proportion of unsaturated fatty acids. Should this condition be found to persist in other specimens, the iodine numbers of these members would afford valuable analytical information. M. J. S.

Assay of Linseed Oil. By HUGO AMSEL (*Zeit. angw. Chem.*, 1897, 369—370).—A controversy with Lippert (this vol., ii, 529). Among other things, the author states that an abnormal solubility of the sample in alcohol, or an increased acidity number, does not necessarily point to an admixture of rosin. L. DE K.

Cause of the Low Iodine Number of Linseed-cake Oil. By G. FASSBENDER and J. KERN (*Zeit. angw. Chem.*, 1897, 331—332).—By means of cold pressure, it is possible to obtain a commercially pure linseed oil from adulterated seed, as the cake retains the greater part of the foreign oils; the amount of foreign *Cruciferæ* in the original material cannot, therefore, be calculated from the iodine number given by the fat extracted from the cake by solvents. L. DE K.

Detection of Vanillin in Resins. By KARL DIETERICH (*Chem. Centr.*, 1896, ii, 364—365; from *Pharm. Centr. Halle*, **37**, 424—427).—To detect vanillin in balsam of Peru, gum benzoin, or storax, the author uses a mixture of equal parts of hydrochloric acid and water, which, on warming, readily takes up the vanillin without dissolving any of the resinous matter; after filtering the hot solution through (animal?) charcoal, the pale yellow liquid is tested with pyrogallol or phloroglucinol. The presence of benzoic or cinnamic acids does not interfere with the test.

To estimate the quantity of vanillin, the hydrochloric extract from 1 kilogram of storax is made strongly alkaline, mixed with 20 grams of hydroxylamine hydrochloride, and heated on the water bath for some hours; the vanillin-oxime thus formed is dissolved by agitating the liquid with ether, the latter is evaporated, the residue treated with boiling water, and the solution put aside to crystallise. It seems to be impossible to completely free the compound from cinnamic acid. The vanillin can be readily calculated from the amount of the oxime.

The author has also worked out and used with some success a colorimetric process depending on the pyrogallol reaction, using solutions of pure vanillin of different strengths for comparison. L. DE K.

New Reagent for Alkaloids. By ADAM JAWOROWSKI (*Chem. Centr.*, 1896, ii, 321—322; from *Pharm. Zeit. Russ.*, **35**, 326—328).—This reagent is prepared by dissolving 0·3 gram of sodium vanadate in 10 c.c. of hot water; when cold, a solution of 0·3 gram of crystallised copper sulphate is added, and then about 8 drops of glacial acetic acid to clear the liquid, which is filtered. The salt of the alkaloid is dissolved in 4—5 c.c. of water if necessary, using a little dilute acetic acid (1 : 18) if it is the free base, and warming gently. One drop of the reagent is added to the solution, and if no precipitate is formed after the lapse of 15 minutes, the mixture is divided into two parts, to one of which a few more drops of the reagent are added, whilst the second portion is heated to boiling; if the liquid becomes turbid in either case, an alkaloid is present.

The following alkaloids are precipitated from solutions containing from 0·01—0·002 per cent.: thebaine, berberine, nicotine, aconitine, strychnine, quinine, quinidine, cinchonidine, cinchonine, brucine, emetine, and apomorphine. On adding excess of acetic acid, the turbidity readily disappears in the case of aconitine, quinine, nicotine, and thebaine; somewhat more slowly in the case of apomorphine (which turns dark blue), berberine, brucine, emetine, and strychnine. The following alkaloids are precipitated from solutions containing at least 0·2 per cent.; morphine, sparteine, papaverine, atropine, narcotine,

and codeine, which appear after 10—60 seconds; also cocaine and hyoscyamine, which only give an opalescence.

The following are not precipitated unless from concentrated solutions: caffeine, colchicine, coniine, cotoine, narceine, pilocarpine, piperine, solanine, theobromine, and veratrine (compare Abstr., 1896, ii, 629). L. DE K.

Estimation of Caffeine in Tea and Coffee. By ALBERT HILGER and A. JUCKENACK (*J. Pharm.*, 1897, [vi], **6**, 184—186 and 190—192; from *Apoth. Zeit.*, 1897, **12**, 145 and 422).—Twenty grams of finely ground coffee or powdered tea is digested at the ordinary temperature with 900 c.c. of water for several hours and then boiled, care being taken to replace the water lost by evaporation. Three hours' boiling is necessary for green coffee, only 1½ hours for roasted coffee or tea. After cooling to 60 to 80°, 7·5—8·0 grams of aluminium acetate in solution (basic aluminium acetate solution of the German pharmacopœia) is run in, and then 1·9 grams of sodium hydrogen carbonate is gradually added while the mixture is well stirred; it is then boiled for 5 minutes, allowed to cool, water added to make the total weight 1020 grams, and filtered. 750 grams of the filtrate—corresponding with 15 grams of coffee or tea—to which 10 grams of dried and finely powdered aluminium hydroxide and a little filter paper have been added, are evaporated to dryness, and the residue dried and extracted for 8 hours with purified carbon tetrachloride. The product obtained after removal of the carbon tetrachloride and drying, is practically pure caffeine, containing at most 2—4 milligrams of impurities. Calcium hydroxide cannot be used in estimating caffeine, as it decomposes part of the alkaloid, according to Schultzen's equation, and converts the rest into caffeidine. Lead hydroxide, obtained by means of ammonia, has no action on caffeine, neither has magnesia.

Caffeine obtained by Trillich and Göckel's method from roasted coffee contains large quantities of impurities, whereas that obtained from green coffee is practically pure. The authors think that the second alkaloid of coffee described by Forster and Riechelmann is a pyridine or a similar base produced during the roasting, since it does not occur in green coffee. J. J. S.

Estimation of Xanthine Bases in Urine. By ROBERT ARNSTEIN (*Zeit. physiol. Chem.*, 1897, **23**, 417—430).—The methods at present principally used (Haycraft's and Camerer's) for the estimation of uric acid and xanthine bases are compared, and the causes of difference discussed. Some modifications are suggested, but an absolutely trustworthy method appears still to be wanting. W. D. H.

Detection of Horse Flesh. By COURLAY and COREMONS (*Chem. Centr.*, 1896, ii, 66—67; from *Ann. de médic. vétérin.*, **10**, 173).—Fifty grams of the fresh and finely divided material is boiled for ¼—½ hour with 200 c.c. of water, the extract filtered through a wetted filter, and a portion of the filtrate treated with a few drops of a solution of 2 parts of iodine, 4 of potassium iodide, and 100 of water. The production of a brown coloration, which disappears at 80° but returns on cooling, indicates the presence of glycogen, and hence of

horse flesh. If the glycogen reaction is masked by the presence of starch, a portion of the filtrate is precipitated with 2—3 volumes of strong acetic acid, and the iodine test applied after filtering. This reaction will distinguish horse flesh from that of oxen, calves, pigs, dogs, and cats, but not from fœtal flesh. The flesh of the masticatory muscles of the horse does not, however, give the glycogen reaction.

M. J. S.

Method for the Examination of Biliary Calculi. By Georges Denigès (*J. Pharm.*, 1897, [vi], 6, 71—72).—A few grains of the powdered calculus is boiled for half a minute or longer with 2 c.c. of glacial acetic acid. Cholesterol may be tested for by placing a drop of the hot solution on an object glass, allowing the acetic acid to evaporate spontaneously for a few minutes, and then examining under the microscope. The drop is then completely evaporated at a gentle heat, immediately wetted with a drop of alcohol, which is likewise allowed to evaporate, and the crystals (rhombohedral plates), after being moistened with water, are examined under the microscope. If the amount of cholesterol present is large, the acetic acid solution, on cooling, will deposit slender, crystalline needles. The presence of cholesterol may be confirmed by Salkowski's colour reaction. Biliary pigments are often detected by the green colour of the acetic acid solution; if this solution is not green, then a small quantity is added to a drop of a 1 per cent. solution of sodium nitrite, a green colour passing through blue to violet indicates the presence of biliary colouring matter. Another test is to add a few drops of hydrogen peroxide to the acetic acid solution when a permanent green coloration is produced. The remainder of the acetic acid solution is evaporated to dryness, and the residue boiled for several minutes with 2 c.c of water and 2 drops of a 25 or 30 per cent. solution of normal potassium oxalate; after filtering and evaporating the filtrate to dryness, the cold residue is mixed with 1 c.c. of alcohol, 1 drop of a sugar solution, and 1 c.c. of sulphuric acid according to Pettenkofer's reaction.

J. J. S.

ERRATA

Vol. LXXII. (Abstr., 1897).

Part I.

Page	Line	
89	22	*for* "$CH_2<\genfrac{}{}{0pt}{}{CH_2\cdot CH_2}{CHPr\cdot CO}>CMe$" *read* "$CH_2<\genfrac{}{}{0pt}{}{CH_2—CH}{CHPr\cdot CO}>CMe$."
100	15*, 14*	*for* "isobutyrylphenylhydrazide" *read* "isobutyrylphenylmethylhydrazide."
136	bottom	,, "bromide" *read* "bromine."
140	4	,, "*ethylic γ-chlorisosuccinate*" read "*ethylic γ-chlorethylisosuccinate.*"
140	6 & 7	,, "ethylamide" *read* "ethylimide."
174	6	,, "$C_8H_{15}N\cdot O\cdot C_7H_{11}N$" *read* "$C_8H_{14}N\cdot O\cdot C_7H_{11}N$."
216	20*	,, "C_4H_4" *read* "C_4H_9."
278	19	,, "$NH_2\cdot C_6H_2(NO_2)<\genfrac{}{}{0pt}{}{—N}{NH}>CMe_2$" *read* "$NH_2\cdot C_6H_2(NO_2)<\genfrac{}{}{0pt}{}{—N}{NH}>CMe$."
282	23*	,, "$(CH_3\cdot CO)_2$" *read* "$(CH_3\cdot CO)_2O$."
284	10	,, "$NH_2\cdot CO\cdot NH_2\cdot C_6H_4\cdot O\cdot CH_2\cdot COOH$" *read* "$NH_2\cdot CO\cdot NH\cdot C_6H_4\cdot O\cdot CH_2\cdot COOH$."
317	19*	,, "$COPr^{\alpha}\cdot COPr_{\alpha}$" *read* "COEt·COEt."
395	4	,, "Allythiocarbimide" *read* "Allylthiocarbimide."
476	18	,, "metanitrobenzoic acid" *read* "metabromobenzoic acid."
,,	8* and 7*	,, "1:2:4:6-chlorotribromaniline" *read* "1:2:4:6-chlorotribromobenzene."
440	20*, 17*	,, "ethoxymethyleneacetate" *read* "ethoxymethyleneacetoacetate."
583	2* and 1*	*should read* "The absorption spectrum of the green colouring matter shows it is not identical with Petit's physostygmine-blue or with Duquesnel's rubreserine."
616, 622	10, 6	*for* "Erhardt" *read* "Ehrhardt."
621	9*	,, "dimethyl" *read* "trimethyl."
647	15	,, "$C_{14}H_2NO_2$" ,, "$C_{14}H_{25}NO_2$."

Part II.

Page	Line	
43	11	*delete* "hydrogen peroxide or."
218	21*	*for* "M" *read* "Ni."
268	8*	*delete* "artificial."
335	14 and 16	*for* "sardines" *read* "tunny."
458	bottom	,, "1897" *read* "1896."
609	21	,, "Herzig" *read* "Herbig."

Index.

Page	Col.	Line	
668	ii	23	*for* "the viscosity of miscible liquids" *read* "the viscosity of mixtures of miscible liquids."
754	i	9	,, "**ψ-Cumenoxyacetyl**" *read* "**ψ-Cumenoxyacetal.**"
793	ii	20*-15*	"**Hexadienes**" *should be under* "**Hexinene,**" page 794, col. ii.

* From bottom.